

INFLUENCE OF CERTAIN REACTION PARAMETERS ON METHANATION OF COAL GAS TO SNG

K.-H. Eisenlohr⁺ F. W. Moeller⁺ and M. Dry⁺⁺

⁺ Lurgi Mineraloeltechnik GmbH., Frankfurt/M., Germany

⁺⁺ South African Coal, Oil and Gas Corporation, Sasolburg, South Africa

INTRODUCTION

Converting coal to a gas which has the same characteristics as natural pipeline quality gas and which is known as substitute natural gas (SNG) is one of the promising possibilities to overcome the increasing energy demand in the United States.

Lurgi pressure gasification of coal and treating and purifying processes for the product gas used in 14 commercial plants are planned to be the basis of a process route to convert coal into SNG 1) 2) 3).

Four different process steps are required in the Lurgi process (Fig. 1):

Pressure gasification of coal
Shift conversion of crude gas
Gas purification by Rectisol
Methane synthesis.

As the methane syntheses process has not yet been applied commercially, it has been of significant importance to demonstrate the technical feasibility of this process step. Therefore two semicommercial pilot plants have been operated for 1 1/2 years.

One plant, designed and erected by Lurgi and South African Coal, Oil and Gas Corporation (SASOL), Sasolburg, South Africa, was operated as a sidestream plant to a commercial Fischer-Tropsch Synthesis. Synthesis gas is produced in a commercial coal pressure gasification plant which includes Rectisol gas purification and shift conversion. So the overall process scheme for production of SNG from coal could be demonstrated successfully.

The other plant, a joint effort of Lurgi and El Paso Natural Gas Corporation, was operated at the same time at Petrochemie, Schwechat, near Vienna, Austria. Starting from synthesis gas produced from naphtha different reaction conditions to those of the SASOL plant have been successfully operated.

The results of two long-term test runs in the SASOL plant in view of the catalyst life under design conditions in a commercial methane synthesis have been published already 3). This paper deals with further test results of both demonstration units concerning the influence of certain reaction parameters which are the basis for flexibility and operability of the Lurgi methanation scheme.

DESIGN OF THE DEMONSTRATION PLANTS

The scheme of a commercial methane synthesis provides a multistage reaction system and hot recycle of product gas. Adiabatic reactors connected with waste heat boilers to remove the heat in form of high pressure steam are used.

In designing the pilot plants major emphasis was placed on the design of the catalytic reactor system. Thermodynamic parameters (composition of feed gas, temperature, temperature rise, pressure, etc.) as well as hydrodynamic parameters (bed depth, linear velocity, catalyst pellet size etc.) are identical to those of a commercial methanation plant. This permits direct upscaling of test results to commercial size reactors, because radial gradients do not exist in an adiabatic shaft reactor.

Arrangement of the semicommercial pilot plants permitted supervision and operation of the plant from a central control panel. The installed safety control system has been successfully tested during several emergency shut-downs with no effect on reactor material and catalyst.

The scheme of the methanation demonstration units can be seen in Fig. 2.

Synthesis gas, after being heated in heater E-1, is mixed with recycle gas. Zinc oxide reactor D-1 serves as an emergency catch pot for sulfur breakthrough from the purification plant. The total feed is heated in heater E-2 and charged to main methanation reactor D-2 with additional steam. Effluent gas from reactor D-2 is cooled in heat exchanger E-3 and cooler E-4, thereby condensing the steam. Part of the reactor effluent gas is recycled, while the rest is reheated in E-3 and fed to final or polishing methanation reactor D-3. Product gas from D-3 is cooled in E-5.

All tests reported here are performed with a special methanation catalyst G 1-85 developed by BASF, Ludwigshafen, for this process. The catalyst with a relatively high nickel content on a carrier was changed to reactors D-2 and D-3 in unreduced form and had to be activated by reduction with hydrogen.

INFLUENCE OF SYNTHESIS GAS COMPOSITION

The influence of synthesis gas composition on conversion, catalyst life, carbon black formation, etc. has been determined in numerous tests. Characteristic parameters for synthesis gas composition are H_2/CO ratio, residual CO_2 content and content of trace components in form of higher hydrocarbons and catalyst poisons.

H_2/CO Ratio

In a commercial shift conversion plant a change in throughput and conversion has to be taken into account and will affect the H_2/CO ratio of the synthesis gas. Therefore the Sasol plant has been operated in three different test runs of more than 1000 hours each with various H_2/CO ratios in synthesis gas to see if there is any effect on operability of methane synthesis. H_2/CO ratios of 5.8; 3.7 and 2.0 were adjusted by varying the mixing ratio of shifted and unshifted coal gas. The test results obtained at a synthesis pressure of 18 kp/cm² are summarized in Tab. 1. The expected equilibrium conversion was achieved in all test runs. A remarkable result has been that there is no difference in the axial temperature profile while operating with synthesis gas with a H_2/CO ratio of 3.7 or 5.8. Adiabatic

endtemperature was reached in both cases in 20% of the catalyst bed depth after 500 operating hours respectively 22% bed depth after 1000 operating hours. Corresponding results have been achieved during a long-term test of 4000 operating hours when the H_2/CO ratio was decreased from 5.8 to 3.8 after 1500 hours and no change in temperature profile and deactivation rate was measurable. 3)

A deviation from these results was measured while operating with a H_2/CO ratio of 2.0. After 500 hours 23% of the catalyst bed depth are needed to reach adiabatic end temperature. The slower reaction rate might be explained by the higher steam content in reactor feed gas and by the fact that part of the CO has to be converted by the relatively slow shift conversion reaction. The negative value of CO_2 conversion shows that CO_2 is formed and not consumed.

In all three tests there was no sign of carbon black formation. Pressure drop over the reactor stays constant during the whole operating period and there was no accumulation of free carbon on catalyst. Analysis of discharged catalyst for free carbon showed only 80 - 90% of the carbon added to the catalyst as pelletizing aid.

Finally it can be said that variation in H_2/CO ratio will not affect operability of an SNG plant using a hot recycle system for methanation as demonstrated in the Sasol plant.

Residual CO_2 Content

The feed gas to Rectisol gas purification will contain 29 - 36 Vol% of CO_2 depending on the rate of shift conversion. The rate of CO_2 to be washed out will be determined by the requirements of methane syntheses and by the need to minimize the cost for Rectisol purification.

For SNG manufacture it is necessary to reduce the hydrogen to a minimum to achieve a high calorific value. This is best realized if synthesis gas, instead of having a stoichiometric composition, contains a surplus of CO_2 which can be utilized to reduce the H_2 content to less than 1 percent according to equilibrium conditions by the CO_2 methanation reaction. The surplus CO_2 has to be removed at the end of the process sequence. It is, of course, also possible to operate a methanation plant with synthesis gas of stoichiometric composition. In this case there is no need for a final CO_2 removal system. The residual H_2 content will be higher and therefore the heating value will be lower, which can be seen by comparing the results of two long-term runs in Tab. 2.

The Sasol plant was operated with a surplus of CO_2 during a long-term test of 4000 hours. 33.4% of the CO_2 in synthesis gas is methanated, while the rest of 66.6% CO_2 leaves the reaction system unconverted. Product gas from final methanation yielded specification grade SNG containing a residual hydrogen of 0.7 Vol% and residual CO of less than 0.1 Vol%. The heating value was 973 BTU/SCF after CO_2 removal to 0.5 Vol% (calc.).

The Schwechat plant was operated in a long-term test of 5000 hours at the same time with a stoichiometric synthesis gas. The residual hydrogen content could be decreased to 2.2 Vol% resulting in a heating value of 950 BTU/SCF when about 1 Vol% nitrogen is present in synthesis gas.

There was no difference in operability and catalyst behaviour (activity and deactivation) recognizable between the two plants. The expected catalyst life time in a commercial plant, calculated from the movement of the temperature profile down the catalyst bed with time, will be in both cases more than 16000 hours at design conditions.

A significant feature of the operation of the two plants was that only a small deviation in feed gas composition is tolerable when using a stoichiometric synthesis gas. Greater deviations in H_2/CO ratio and residual CO_2 content of the feed gas will cause serious problems regarding SNG specification. The conclusion is only reasonable when there are no high requirements for SNG specification.

Higher-Hydrocarbon Content

Coal pressure gasification gas, after purification in a Rectisol unit, will contain higher hydrocarbons in the C_2-C_3 range of 0.2 to 0.6 Vol%. The results of an analytical examination during all test runs showed that the used nickel catalyst has a good gasification or hydrogenation activity. Unsaturated hydrocarbons such as ethylene and propylene are hydrogenated completely while the saturated hydrocarbons such as ethane and propane are converted to methane up to equilibrium concentrations of 50 ppm ethane and 5 ppm propane.

Catalyst Poisons

It is well known that sulfur, chlorine etc. are strong poisons for nickel catalyst. Chlorine was not detectable in synthesis gas downstream Rectisol in the Sasol plant. The total sulfur content in the same gas, in form of H_2S , COS and organic sulfur compounds, has been 0.08 mg/Nm^3 on the average with maximum values of 0.12 mg/Nm^3 total sulfur at average H_2S content of 0.03 mg/Nm^3 .

The effect of sulfur contamination on catalyst activity was examined in an extra test run in the Sasol plant. The results can be seen from Fig. 3, where conversion in 6.3% and 23.8% of the total catalyst bed as an indirect criterion of catalyst activity is plotted versus operating time.

In the first operating period (750 - 950 h) the plant was run with the ZnO emergency catchpot on line. Sulfur could be decreased to 0.04 mg/Nm^3 total sulfur and $0.02 \text{ mg/Nm}^3 H_2S$. The conversion in the first 6.3% of the catalyst bed decreased from 50% to 46% while no change in conversion was detectable in the first 23.8% of the bed.

No change in deactivation was measured when in the second operating period (950 - 1230 h) ZnO reactor D-1 was by-passed. The conversion in the first 6.3% of the catalyst bed came down from 46% to 42%.

In the third operating period (1230 - 1380 h) a breakthrough of $4 \text{ mg/Nm}^3 H_2S$ in synthesis gas was simulated, causing an enormous activity loss. The point of reaching adiabatic end temperature in the catalyst bed went down from 22% to 44% bed depth, while the conversion in the first 23.8% of the bed came down from 100% to 78%. Operating 150 hours with $4 \text{ mg/Nm}^3 H_2S$ corresponds to one year operation with 0.08 mg/Nm^3 total sulfur in the feed gas to methanation.

These tests permit the simplified conclusion that synthesis gas purified in a Rectisol unit can be charged directly to the methanation plant without severe problems concerning sulfur poisoning of the nickel catalyst. But to cope with a sudden sulfur breakthrough from Rectisol as a result of maloperation a commercial methanation plant should be operated with a ZnO emergency catchpot on line.

INFLUENCE OF TEMPERATURE AND PRESSURE

The selection of optimal reactor inlet and outlet temperature is influenced by the catalyst activity and catalyst stability and by the need to minimize operating and investment costs.

Using a catalyst like G 1-85 of BASF inlet temperatures in the range of 260°C to 300°C or even lower will be quite acceptable as indicated by the test reported in Tab. 2. The final decision on design inlet temperature is effected by engineering requirements.

The long-term tests in the Sasol plant as well as in the Schwechat plant have been operated with outlet temperatures of 450°C. But both plants also have been operated with higher load causing reactor outlet temperatures of 470°C or even higher. In comparison with the test run at 450°C there was no increase in deactivation rate detectable, which demonstrates the thermostability of the catalyst. From the viewpoint of thermostability outlet temperatures in the range of 450°C - 500°C are acceptable. Further consideration concerning possibility of overload operation, SNG specification to be achieved in final methanation, end of run conditions, cost of reactor material, etc. will affect the selection of optimal outlet temperature.

The influence of total pressure is limited. For reasons of SNG specification a relatively high pressure is preferred but compression of synthesis gas compared with final SNG compression turned out to be uneconomical. The pressure in methanation is governed by the pressure of gasification and the pressure drop across upstream plants.

INFLUENCE OF STEAM

Apart from actual synthesis tests extensive investigations were made on fresh and used catalyst to determine the effect of steam on catalyst activity and catalyst stability by measurement of surface areas. While the BET area 4) is a measure of the total surface area, the volume of chemisorbed hydrogen is a measure of the amount of exposed metallic nickel area only and therefore should be a truer measure of the catalytically active area.

The test results of H₂ chemisorption measurement are summarized in Tab. 3. For the fresh reduced G 1-85 an activity equivalent to 11.2 ml/gr was determined. When this reduced catalyst is treated with a mixture of hydrogen and steam, it loses 27% of its activity. This activity loss is definitely caused by steam as a catalyst treated 4000 hours in final methanation with a nearly dry gas showed no activity loss. In the first 1000 operating hours the catalyst loses again 33% of its activity in the top section and 16% in the bottom section of the reactor. This should be called loss of start activity. In the next 3000 operating hours the activity loss has been extremely low. Catalyst has achieved its stabilized standard activity.

The activity loss measured here is caused by recrystallisations as proved by nickel crystallite size determination on the same catalyst samples by scanning electron microscopy.

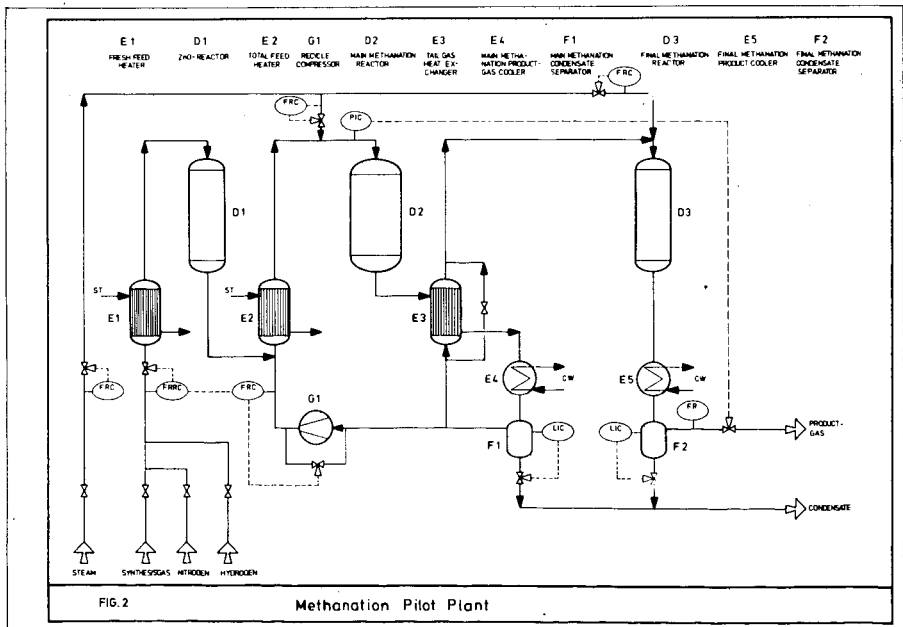
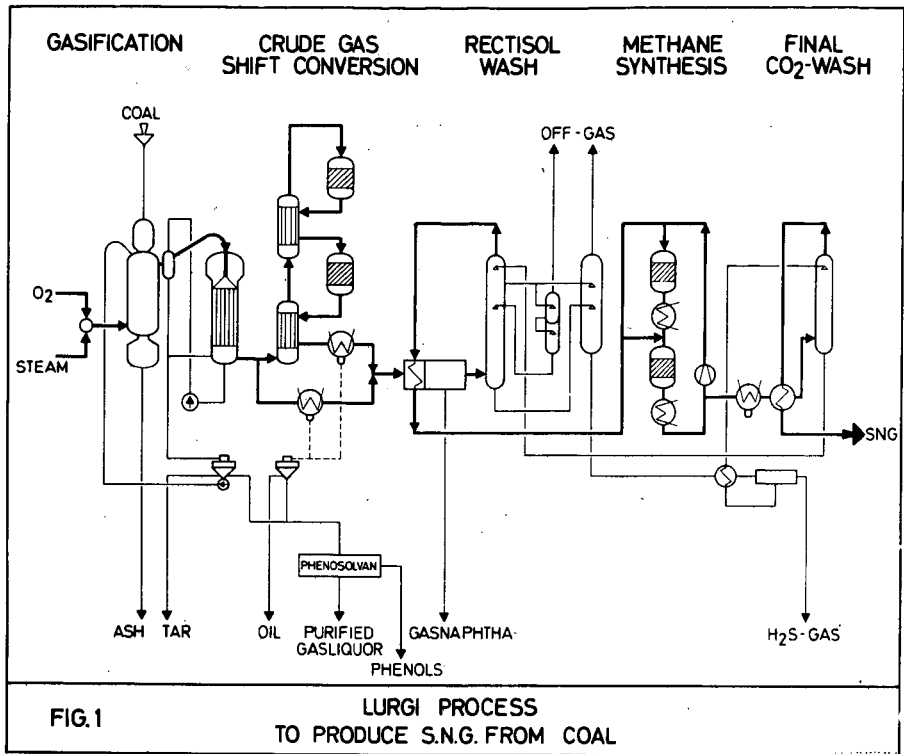
These tests have shown that the catalyst used in demonstration plants has only little tendency to recrystallise or sinter after steam formation and loss of start activity.

CONCLUSION

These tests have been performed to establish the limits in flexibility and operability of a methanation scheme. The two demonstration plants have been operated to find optimal design parameters as well as the possible variation range which can be handled without affecting catalyst life and SNG specification. Using a hot recycle methanation system the requirement for synthesis gas concerning H_2/CO ratio, CO_2 content, higher hydrocarbon content are not fixed to a small range, only the content of poisons should be kept to a minimum. The catalyst has proved its chemostability and resistance against high steam contents, resulting into an expected life of more than 16 000 hours.

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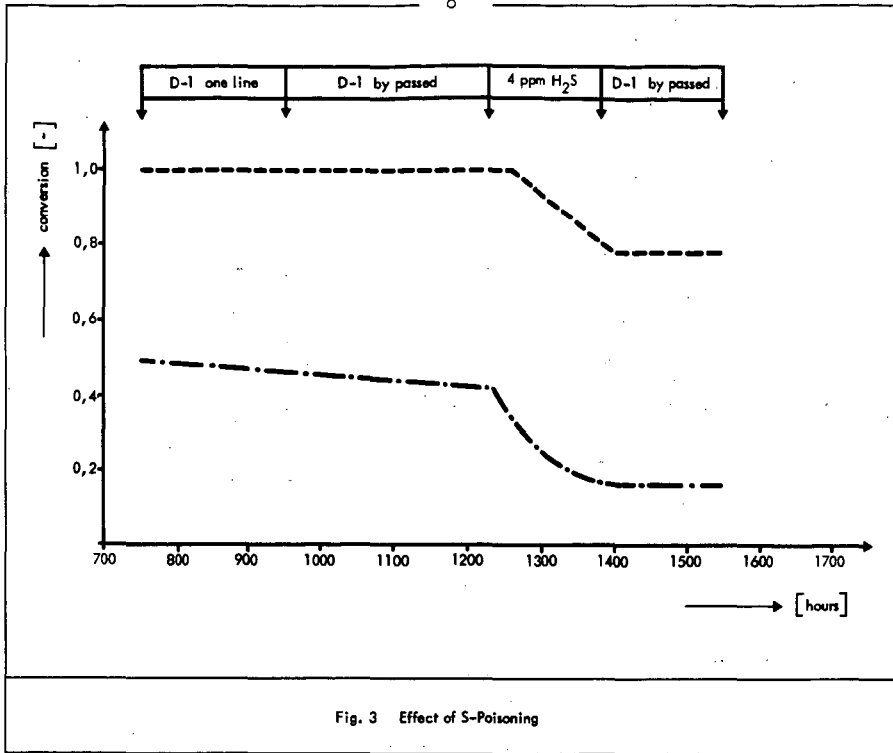


Table 1

	$H_2/CO = 5.8$			$H_2/CO = 3.7$			$H_2/CO = 2.0$		
	Syngas	Feed to D-2	Effluent gas D-2	Syngas	Feed to D-2	Effluent gas D-2	Syngas	Feed to D-2	Effluent gas D-2
Pressure (kg/cm^2)		18.0			18.0			18.0	
Temperature ($^{\circ}C$)	270	300	450	270	300	450	270	300	450
Gas composition									
CO_2 Vol%	16.6	20.5	22.1	9.4	15.4	17.2	0.8	14.6	19.0
CO "	10.7	3.4	0.4	16.6	4.1	0.4	28.6	7.2	0.4
H_2 "	62.0	23.9	8.7	62.0	20.6	8.4	56.6	22.7	12.0
CH_4 "	9.8	50.7	67.0	10.8	57.7	71.6	12.3	52.8	65.5
C_2^+ "	0.2	0.1	<0.1	0.2	0.1	<0.1	0.2	0.1	<0.1
N_2 "	0.7	1.4	1.7	1.0	2.1	2.4	1.5	2.6	3.0
H_2O Nm^3/Nm^3	-	0.417	0.584	-	0.387	0.501	-	0.722	0.852
Total conversion									
U_{CO_2} %		48.3			23.7			1076.3	
U_{CO} %		98.4			99.0			99.3	
U_{H_2} %		94.1			94.3			89.5	
Bed depth needed for total conversion %									
500 hrs		20			20			23	
1000 hrs		22			22			25	

Table 2

	Sasol plant					Schwechat plant				
	Main methanation			Final methanation		Main methanation			Final methanation	
	Syngas	Feed D 2	Effluent gas D 2	Feed D 3	Effluent gas D 3	Syngas	Feed D 2	Effluent gas D 2	Feed D 3	Effluent gas D 3
Pressure (kp/cm ²)	-	18.0	-	-	-	-	16.3	-	-	-
Temperature (°C)	270	300	450	260	315	-	290	440	283	345
Gas composition										
CO ₂ Vol%	13.0	19.3	21.5	21.5	21.3	5.1	4.4	4.1	4.1	1.8
CO Vol%	15.5	4.3	0.4	0.4	<0.1	14.4	4.0	0.1	0.1	<0.1
H ₂ Vol%	60.1	41.3	7.7	7.7	0.7	61.6	25.7	12.1	12.1	2.2
CH ₄ Vol%	10.3	53.3	68.4	68.4	75.9	18.9	65.9	83.7	83.7	96.0
C ₂ + Vol%	0.2	0.1	<0.1	<0.1	<0.1	-	-	-	-	-
N ₂ Vol%	0.9	1.7	2.0	2.0	2.0	-	-	-	-	-
H ₂ O (Nm ³ /Nm ³)	-	0.37	0.50	0.04	0.08	-	0.349	0.481	0.061	0.123
Total Conversion										
U _{CO₂} (%)			33.4						86.1	
U _{CO} (%)			99.9						99.9	
U _{H₂} (%)			99.5						98.6	

Table 3:

	H ₂ -Adsorption (ml/gr)
Fresh reduced catalyst G 1-85	11.2
H ₂ /H ₂ O-Treatment	8.0
Used catalyst out of main methanation	
1000 hrs	4.4 (top bed) 6.4 (bottom bed)
4000 hrs	4.0 (top bed) 6.2 (bottom bed)
Used catalyst out of final methanation	
4000 hrs	11.0 (middle bed)

SYNTHESIS OF METHANE IN HOT GAS RECYCLE REACTOR--PILOT PLANT TESTS

W. P. Haynes, A. J. Forney, J. J. Elliott, and H. W. Pennline

U.S. Bureau of Mines, 4800 Forbes Avenue, Pittsburgh, Pa.

INTRODUCTION

Development of large-scale catalytic methanation reactors is necessary to complete the commercialization of plants for converting coal to substitute natural gas. Major objectives in developing a catalytic methanation system are to achieve efficient removal of the heat of reaction so as to minimize thermal deactivation of catalyst and to minimize catalyst deactivation by other causes such as chemical poisoning and structural changes. The hot gas recycle reactor, where large quantities of partially cooled product gas are circulated thru the catalyst bed, affords one satisfactory method of removing large amounts of heat from the catalyst surface. Early Bureau of Mines experiments with the hot gas recycle reactor, however, had short catalyst lives, on the order of 200 hours. (1) ^{1/} The work described in this report attempts to extend the life of the catalyst in the hot gas recycle reactor system, to determine the effects of some of the process variables, and to compare the performance of a bed of pelleted nickel catalyst against that of a bed of parallel plates coated with Raney nickel.

PILOT PLANT DESCRIPTION

The reactor in the hot gas recycle pilot plant was constructed of type 304 stainless steel 3 inch schedule 40 pipe, 10 feet long, flanged at each end. In three experiments (HGR-10, 12, and 14), the catalyst bed consisted of grid assemblies of parallel, type 304 stainless steel plates, that had been flame spray coated with Raney nickel. The grid assemblies, each 6 inches long, were stacked to the desired bed height and conformed to the inside diameter of the reactor. Grid plates were aligned perpendicular to the plate alignment of adjacent grids. Prior to assembly, each plate was sand-blasted on both sides, flame sprayed with a bond coat, and finally flame sprayed with the Raney nickel catalyst. Thickness of the Raney nickel coating was approximately 0.02 inches. In experiment HGR-13, the reactor was charged with 1/4" pellets of a commercial grade precipitated nickel catalyst instead of the parallel plates coated with Raney nickel. Physical properties of the catalyst beds are shown in table 1.

The basic hot gas recycle reactor scheme is shown in the simplified flowsheet of figure 1. The main reactor containing the parallel plate grid assemblies is the one under study in this report. The second stage reactor, an adiabatic reactor charged with a precipitated nickel catalyst, was operated at intermittent periods; its operation will be discussed in a later report. Additional heat exchangers, not shown in the flowsheet, were used in the pilot plant to compensate for system heat losses, to achieve a measure of heat recuperation, and to control the gas temperature into the hot gas compressor and into the main reactor. Cooling of the main catalyst bed is achieved by direct transfer of the reaction heat to the slightly cooler gas stream flowing through the bed. Recycle stream is appropriately cooled before returning to the reactor. The hot recycle stream may be cooled either directly without condensation or by cooling a portion of the recycled product gas sufficiently to condense out the water vapor and then returning the resulting cold recycle gas along with the hot recycle gas. After undergoing a final heat exchange, the mixture of the cooled recycle gas and the fresh feed gas comprise a feed to the hot gas recycle

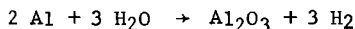
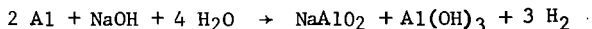
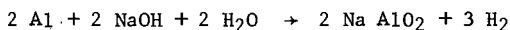
^{1/} Underlined numbers in parenthesis refer to references at the end of this paper.

reactor at a controlled temperature that may be 50 to 150° C lower than the reactor outlet temperature, depending upon the total amount of gas recycled and the amount of heat exchange.

Charcoal absorption towers (not shown in the flowsheet) were used to keep the sulfur content in the fresh feed gas to less than 0.1 ppm, in equivalent volume of H₂S.

CATALYST PREPARATION

The metal plates to be coated with Raney nickel were type 304 stainless steel. The surfaces of the plates were prepared by sand-blasting with an iron-free grit and then flame spraying on a light coat of bonding material, about 0.006 inches thick. After the surface was bond coated, the Raney nickel alloy powder (80-100 mesh) was flame sprayed on to the desired thickness. The plates were assembled in parallel, inserted in the reactor, and then activated. Activation of the Raney nickel involved passing a 2 wt. per cent solution of NaOH through the catalyst bed to dissolve away the aluminum phase and leave a spongy surface of highly active free nickel. Activation was stopped after 70 per cent of the aluminum in the Raney alloy was reacted. The remaining unreacted alloy is believed to provide a base upon which the activated nickel remains anchored. The extent of reaction was determined by measuring the hydrogen evolved according to the following three reactions, all of which evolve 3 moles of H₂ for every 2 moles of Al reacted:



After the aluminum was reacted, the catalyst was washed with water which had a pH of about 6.8 until the pH of the effluent water reached about 7.2. After the catalyst was activated and washed, it was always kept under a hydrogen atmosphere until it was put into methanation service at the desired operating pressure and temperature. Before cooling the catalyst to take it out of service, the reactor was purged with hydrogen. It was kept in a hydrogen atmosphere during cooling, depressurizing, and stand-by condition.

In experiment HGR-13, the commercial grade precipitated nickel catalyst was in a reduced and stabilized condition when it was charged into the reactor. No special activation treatment was needed. It was, however, kept under a hydrogen atmosphere at all times until the temperature and pressure of the system was brought to synthesis conditions at which time the synthesis feed gas was gradually fed into the system to start the run.

PROCEDURES AND RESULTS

General

Experiments HGR-10, 12 and 14 were conducted with the flame sprayed Raney nickel catalyst. Experiment HGR-13 used the pelleted precipitated catalyst to compare its performance with that of catalyst used in HGR-14. Reactor conditions as a function of stream time for experiments HGR-10, 12, 13, and 14 are graphically presented by computer print-out in figures 2, 4, 6, and 8, respectively. Corresponding carbon monoxide concentrations and heating values of the product gases and the yields of methane produced per pound of catalyst used are presented graphically as a function

of stream time in figures 3, 5, 7, and 9. The total recycle ratio was calculated on the basis of stream analyses, and fluctuated widely because of the high sensitivity of the calculated values to small changes in stream analyses. All runs were made at 300 psig.

The major process parameters are presented in tables 2, 3, 4, and 5 at selected periods in experiments HGR-10, 12, 13, and 14, respectively. Carbon recoveries shown for these periods ranged from 63 per cent to 91 per cent. Most of the losses occurred in connection with the recycle compressor system and correspondingly decreased the volume of product gas metered. Such losses, however, did not significantly affect the incoming gas to the main reactor or the performance of the reactor.

Experiment HGR-10

Experiment HGR-10 operated at 300 psig with recycle ratios being varied to give temperature rises across the catalyst bed ranging from 50° to 150° C. Temperature control was excellent. Total operating time was relatively short at 910 hours. The initial carbon monoxide concentration in the product gas at 0.3 per cent was higher than the desired value of less than 0.1 per cent. Over the entire experiment, the average rate of catalyst deactivation, expressed as increase in the per cent carbon monoxide in the dry product gas per mscf methane produced per pound of catalyst charged, was 0.23 per cent/mscf/lb. This is a high rate of deactivation compared with the value of about 0.009 per cent/mscf/lb. obtained with Raney nickel catalyst in a tube-wall methanator test (TWR-6). (2) Because the experiment was of short duration, the resulting production of methane per pound of catalyst in HGR-10 was low at about 11.8 mscf/lb. as compared with 177 mscf/lb. in tube-wall reactor test TWR-6.

One probable reason for the relatively poor catalyst performance in experiment HGR-10 was the excessively large deposits of iron and carbon on the catalyst surface. Table 6 shows iron and carbon concentrations of 22.0 and 13.4 weight per cent, respectively, on the catalyst near the gas inlet, and 0.8 and 1.9 weight per cent, respectively, on the catalyst near the gas outlet. It is suspected that the large deposit of iron resulted from the decomposition of iron carbonyl carried in from other parts of the reactor system, and the deposited iron in turn favored the formation of free carbon from the incoming carbon monoxide.

Experiment HGR-12

As shown in table 1, the catalyst bed for experiment HGR-12 was the same as that used in experiment HGR-10, except that the coat of Raney nickel used in HGR-12 was slightly thinner than that used in HGR-10. The objective in HGR-12 was to increase catalyst life. The methane produced per pound of catalyst was 39.5 mscf after a total operating time of about 1400 hour (See figure 5). The overall average rate of catalyst deactivation, 0.091 per cent per mscf per lb., was about 40 per cent of that for experiment HGR-10, but still 10 times greater than that of experiment TWR-6. The carbon monoxide concentration in HGR-12 increased from 0.1 per cent at the start of the experiment, to 3.7 per cent at the end of the experiment.

In general, the rate of deactivation was much lower at the lower fresh gas feed rate than at the higher feed rates. For example, during the period between 600 hours and 800 hours stream time, at the lower feed rate of about 206 scfh, the rate of deactivation was 0.022 per cent/mscf/lb. as compared with a deactivation rate of 0.143 per cent/mscf/lb. for the period between 100 hours and 400 hours where the fresh feed rate was about 386 scfh.

The cold gas recycle ratio values shown in figure 4 are metered values and are more consistent than the hot gas recycle and total gas recycle ratio values which, as explained earlier, were calculated from gas analyses. Although the calculated total recycle gas flow rate was erratic, the catalyst bed temperatures were uniform and easily controlled by varying the recycle rate and its temperature level. The uniformity of the catalyst bed temperature, as shown by figure 4, indicates that the actual recycle rate was much more uniform than indicated by the calculated values. The data plotted in figures 4 and 5, indicate that between the stream time of 260 hours and 460 hours, raising the maximum temperature of the catalyst bed from 350° C to 410° C did not significantly change the trend of increasing carbon monoxide concentration in product gas. However, this trend in carbon monoxide concentration was reversed during the subsequent period between 467 and 539 hours when the carbon monoxide concentration in the product gas decreased from 2.0 to 1.7 per cent (dry). This decrease in carbon monoxide concentration is attributed mainly to the ratio of total recycle gas to a fresh gas being decreased from about 20:1 to about 8:1 with an attendant increase in residence time. The decrease in total recycle ratio was achieved by reducing the hot gas recycle ratio to about 5:1 while leaving the cold gas recycle ratio constant at 3:1. The water vapor concentration in the mixed feed to the reactor correspondingly was decreased slightly from 5.5 per cent to 3.7 per cent and the resulting temperature spread across the catalyst bed increased from about 51° C to 112° C. Table 3 shows the wet analyses of the product gas during operation with the lower recycle ratio of 8:1 at 539 hours stream time.

After experiment HGR-12 was ended, samples of the spent catalyst were taken from various locations in the bed, and surface areas (B.E.T.), pore volumes and distribution of pore radii were determined for each sample. The results are shown in table 7 as a function of distance from the gas inlet end of the catalyst bed. Additional catalyst information such as x-ray analysis, chemical analysis, and metal surface area determined by chemisorbed hydrogen are presented in table 8 for spent catalyst at the gas inlet and outlet. The B.E.T. surface areas are about one-half that of freshly activated Raney nickel where the surface area is as high as 64 m²/gm.

Special catalyst activities expressed as per cent CO converted to methane were determined in a thermogravimetric analyzer for samples of spent catalyst taken at 0, 6, and 60 inches from the gas inlet; corresponding CO conversions were 0.0, 0.9, and 18 per cent. The catalyst nearest the gas outlet--when compared with catalyst at the gas inlet--was the most active and had the lowest carbon content, the larger pore radii with 96 per cent of its pore volume having radii greater than 60 Å, the lowest B.E.T. surface area (19.5 m²/gm) and the largest free metal surface (4.9 m²/gm). These observations are all consistent if one assumes that the combination of finer pore structure and higher B.E.T. surface area found at the gas inlet side of the bed is indicative of a higher carbon concentration and that the nickel pore radii are larger than that of the amorphous carbon deposit.

Experiment HGR-13

In experiment HGR-13, a two foot bed of commercial catalyst was tested as a packed bed of 1/4 inch pellets. (See table 1 for bed properties). This test was made for comparison with a similar test (HGR-14) using a catalyst bed of parallel plates sprayed with Raney nickel. The experiment also was to show the effect of varying the fresh feed rate from a space velocity of 2000 to 3000 hours⁻¹, where space velocity is based on scfh of gas at 1 atm and 32° F per cubic foot of catalyst bed.

Major process conditions for experiment HGR-13 are plotted against stream time in figure 6. The total recycle ratio was held relatively constant at about 10:1 resulting in a constant temperature-rise of about 100° C across the catalyst bed

(300° C at the inlet and 400° C maximum). Near the end of the experiment, the cold recycle ratio was varied between the value of 8:1 and 1:1. The experiment was ended at 1368 hours.

As shown in figure 7, the carbon monoxide concentration in the dry product gas ranged from about 0.02 per cent at the start to 1.2 per cent at 840 hours, and decreased to 0.88 per cent at 1368 hours, at the end of the run. The total methane produced per lb. of catalyst was about 11.5 mscf/lb. Heating value of the product ranged from 885 to about 960 Btu/scf.

The overall deactivation rate expressed as per cent carbon monoxide increase per mscf methane produced per pound of catalyst was about 0.076. During the course of the experiment, as the fresh gas rate was varied from about 210 scfh to 320 scfh and finally back to 210 scfh, deactivation rates corresponding to those feed rates were 0.014, 0.222 and 0.079. Thus, the deactivation rate was increased irreversibly by increasing the fresh gas rate.

Typical operating data from selected periods in experiment HGR-13 are presented in table 4. Period 6, 168 hours stream time, is typical of conditions at the initial part of the experiment while period 54 is representative of conditions at the end of the experiment. Comparison of period 20 with period 6 indicates that very little change in performance occurred over that span of 336 hours of operation; for example, the decrease in conversion of (CO + H₂) in the fresh feed gas was very slight, decreasing from 98.0 per cent to 97.9 per cent. Comparison of period 20 with period 22, shows typical effects of increasing the fresh feed rate from a space velocity of 2110 hr⁻¹ to 3020 hr⁻¹. Conversion of H₂ + CO in the fresh feed, for example, dropped from 97.9 per cent to 97.1 per cent. Data in period 34 shows a further drop in performance which may be attributed to continued operation at the higher fresh feed rate of 320 scfh or space velocity of 3120 hr⁻¹.

After the fresh feed rate was returned to the lower rate of 211 scfh, a comparison of carbon monoxide in the product gas in period 37 (0.4 per cent) with that in period 20 (0.1 per cent) shows that the catalyst had definitely lost activity with time. However, this activity loss is not evident in the respective heating values of 933 and 926 Btu/scf, for periods 37 and 20 because the product gas in period 37 was less diluted with excess hydrogen than was the product gas in period 20. This is confirmed by the H₂/CO in the fresh feed gas; H₂/CO=3.01 for period 37 and 3.24 for period 20.

X-ray defraction analysis of the spent catalyst presented in table 8 show the nickel to be present only in the metallic state. Chemical analyses also presented in table 8 indicate very little difference in composition of catalyst at the gas inlet and at the gas outlet.

Experiment HGR-14

The reactor was packed with 2 feet of parallel plates sprayed with Raney nickel as described in table 1. Spraying and activation of the catalyst was the same as described under catalyst preparation. Operating conditions were maintained practically the same as they were for experiment HGR-13, except for the periodic changes in the cold gas recycle ratio. Figure 8 shows reactor conditions in experiment HGR-14 as a function of time on stream and figure 9 presents the resulting carbon monoxide concentration, heating values, and methane produced per pound of catalyst.

At the start of the experiment, the carbon monoxide concentration in the product gas was very low, less than 0.01 per cent. The unusually high value (0.71 per cent) shown at 186 hours stream time is due to analytical error. At the end of the experiment, after 2307 hours stream time, carbon monoxide in the product gas had increased

to 0.93 per cent (dry basis) and total methane produced per pound of catalyst was 32 mscf/lb.

The average catalyst deactivation rate over the entire experiment was 0.0291 per cent/mscf/lb. The rate of deactivation during the initial 462 hours operation at a fresh feed space velocity of about 2090 hr^{-1} (216 scfh) was very low at 0.0017 per cent/mscf/lb.; from about 500 hours to 841 hours at about 2990 hr^{-1} space velocity, the rate of deactivation increased to 0.040 per cent/mscf/lb. Catalyst deactivation rates during HGR-14 are shown below for various operating periods and fresh feed space velocities:

Nominal Fresh Feed Space Velocity, hrs^{-1}	Stream Period, hrs		Catalyst Deactivation Rate, per cent/mscf/lb
	From	To	
2000	0	462	0.00166
3000	462	841	0.0396
2000	841	1058	0.0027
2000	1058	1760	0.0187
2000	1760	2180	0.0821

As noted previously in experiment HGR-13, the deactivation rate increased significantly when the fresh feed space velocity was increased from 2000 hr^{-1} to 3000 hr^{-1} . During the period 841 to 1058 hrs., the fresh feed space velocity was returned to 2000 hr^{-1} and the cold gas recycle ratio was increased from about 3:1 to about 9:1 to give a low deactivation rate of 0.0027 per cent/mscf/lb. When the cold recycle ratio was returned to about 3:1 in the period 1058 to 1760 hrs., the rate of catalyst deactivation was increased to 0.0187 per cent/mscf/lb. After 1760 hours, the unit was shut-down and put in standby condition under a hydrogen atmosphere. After the unit was restarted, the deactivation rate had increased greatly to 0.0821 per cent/mscf/lb., indicating that the increase in deactivation rate was associated with this particular shutdown. The fact that this experiment previously had undergone three unscheduled shutdowns at 215, 798, and 894 hours with no adverse effect on performance, indicates that some unknown factor unique to the 1760 hour shutdown was responsible for the subsequent rapid decline in activity.

The operating data shown in table 5 were selected to provide more detailed information on points of special interest in the experiment as follows:

Period 4.....represents performance at 2000 hr^{-1} fresh gas space velocity and 3:1 cold recycle when the catalyst is fresh.

Period 15.....represents performance at 2000 hr^{-1} space velocity before changes to 3000 hr^{-1} .

Periods 17 and 26...represent the beginning and end of the 3000 hr^{-1} space velocity operation.

Period 34.....represents operation at 2000 hr^{-1} space velocity and a high value of the cold gas recycle ratio (9.59:1).

Periods 37 and 62...represent the beginning and end of an operating period later in the experiment with 2000 hr^{-1} space velocity and 3:1 cold recycle ratio.

Periods 62 and 64...provide further comparison of the effect of increasing the cold recycle ratio from 3:1 to 10:1.

Period 76.....represents performance after a long period of operation, 2207 hours.

X-ray analysis of the spent catalyst (table 8) showed metallic nickel and nickel carbide, Ni_3C , in catalyst near the gas inlet and only metallic nickel in catalyst near the gas outlet.

DISCUSSION OF RESULTS

Operability

All four series of experiments have proven that the hot gas recycle methanation system is a usable and operable system. With a total gas recycle ratio of about 10:1 and with CO concentrations as high as 4.3 per cent (wet basis) in the mixed feed entering the catalyst bed, temperature control was excellent; no hot spots developed. It appears likely that lower recycle ratios, although it is not known how much lower, could be used successfully with an attendant increase in inlet CO concentration and an increase in temperature rise across the bed. Further testing is required to determine the limit in decreasing the total recycle ratio and the effect of such a decrease on the catalyst life.

Flame Sprayed Raney Nickel Plates vs Pellets of Precipitated Catalyst in a Packed Bed

Results of experiment HGR-13 and HGR-14 have shown that the performance of the plates sprayed with Raney nickel catalyst was significantly better than that of the precipitated nickel catalyst pellets. The sprayed plates were better in that they yielded the higher production of methane per pound of catalyst, the longer catalyst life or lower rate of deactivation, the lower carbon monoxide concentration in the product gas, and the lower pressure drop across the catalyst bed.

One of the reasons for developing the parallel plate catalyst was to reduce the pressure drop across the catalyst bed and consequently reduce power costs for circulating the recycle gas. Pressure drop measurements across the 2 foot long catalyst beds are listed below:

		<u>Pressure Drop</u>	<u>Inches Water</u>
Nominal Space Velocity, hr^{-1}		Exp. HGR-14	Exp. HGR-13
Fresh Feed	Total Feed	(Parallel plates)	(1/4" pellets)
2000	22,000	2.0	28
3000	33,000	2.7	49

The above data show that the pressure drop across the parallel plates is in the order of $1/15^{\text{th}}$ that across the bed of pelleted catalyst.

The bed of parallel plates coated with Raney nickel catalyst was much more reactive than the bed of precipitated nickel. This was shown by the generally lower carbon monoxide concentration in the product gas during operation with the parallel plate bed; for example, after about 450 hours stream time, carbon monoxide in the product was 0.01 per cent for the bed of sprayed Raney nickel (HGR 14) and 0.05 per cent for the bed of precipitated nickel catalyst (HGR 13).

The higher reactivity of the plates coated with Raney nickel is further illustrated by the plots of catalyst temperature vs bed length shown in figure 10. The maximum bed temperature (indicating near completion of methanation) is consistently reached within a shorter distance from the gas inlet and the slope of the curves are correspondingly steeper for the more reactive bed of parallel plates coated with Raney nickel than for the bed of precipitated nickel.

The initial reactivities of the catalyst beds in experiments HGR-13 and 14 are considered to be satisfactorily high; however, the overall rate of deactivation of the bed of Raney nickel catalyst (0.029 per cent/mscf/lb) was much lower than that of the precipitated catalyst (0.076 per cent/mscf/lb). This, consequently, has resulted in a longer catalyst life (2307 vs 1368 hours) and a higher yield of methane per pound of catalyst (32.0 vs 11.5 mscf/lb) for the Raney nickel catalyst over that for the precipitated nickel catalyst.

Other precipitated nickel catalysts have been developed recently that reputedly are superior to that used in experiment HGR-13. These catalysts will be evaluated in the near future, as well as other forms of Raney nickel.

Effects of Cold Gas Recycle and Approach to Equilibrium

Product gases resulting from various cold recycle ratios are shown in table 9. For the experiments shown, a decrease in the cold recycle ratio resulted consistently in an increase in concentration in the product gas of water vapor, hydrogen, and carbon dioxide and a decrease in methane. These trends may be noted in experiment HGR-12 as the cold recycle ratio decreased from 8.7:1 to 1.2:1, in experiment HGR-13 as the cold recycle ratio increased from 1.0:1 to 9.1:1, and in experiment HGR-14 as the cold gas recycle ratio decreased from 3.0:1 to 1.0:1. The above-mentioned trends indicate that the water gas shift reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ was sustained to some degree. Except for the 462 hour period of experiment HGR-14, the apparent mass action constants for the water gas shift reaction based on the product gas compositions shown in table 9 remained fairly constant and ranged between 0.57 and 1.6. These values are much lower than the value of 11.7 for equilibrium conversion at 400° C. At 462 hours in experiment HGR-14, the apparent mass action constant for the shift reaction was 0.075, which represents a much greater departure from equilibrium than that encountered in the other periods shown in table 9. The apparent mass action constant for the methanation reaction $3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ at 462 hours in experiment HGR-14 was 2650 which was a much closer approach to the 400° C equilibrium value of 1.7×10^4 than was achieved by the other test periods shown in table 9. This greater dominance by the methanation reaction while the catalyst is still relatively fresh probably caused the greater departure from equilibrium observed in the shift reaction during the early part of the experiment, at the 462 hour period.

Catalyst Deactivation

In this series of hot gas recycle experiments, the sulfur content in the feed gas was held very low, generally less than 0.1 ppm. Catalyst deactivation caused by sulfur poisoning is, therefore, considered negligible. On the other hand, the iron deposited on the catalyst in experiments HGR-10 and to a lesser extent in experiments HGR-12 and 14, is suspected of promoting carbon formation and subsequent fouling and deactivation of the catalyst. Iron concentrations of 5 mg/mscf have been determined in the recycle stream indicating the presence of iron carbonyl. Iron to nickel ratio in the fresh Raney nickel is about 2.4 Fe:1000 Ni, but the ratios are significantly higher for the spent Raney nickel catalyst. Based on analyses shown in table 8, Fe:Ni ratios for the spent Raney nickel catalysts of experiments HGR-12 and 14 ranged from 5.2 Fe:1000 Ni to 14.8 Fe:1000 Ni with the higher iron concentrations generally resulting in greater carbon deposition. The same trend was observed in experiment HGR-10.

Nickel carbide was detected on the catalyst in experiment HGR-14 and is another compound suspected of deactivating Raney nickel catalyst. However, inasmuch as the shutdown involved purging with hydrogen while the catalyst was hot, the presence of nickel carbide is contrary to Steffgen's (3) findings on a TGA apparatus that nickel

carbide is not stable under hydrogen at temperatures above 280° C. More information on nickel carbide formation is needed.

The metal surface area at the inlet end of the catalyst bed of experiment HGR-12 being smaller than at the outlet end indicates that a decrease in nickel metal sites is part of the deactivation process. Sintering of the nickel is one possible mechanism, but carbon and carbide formation are suspected major causes. The loss of active Raney nickel sites could also conceivably result from diffusion and subsequent alloying of residual free aluminum from unleached catalyst with the free nickel to form an inactive material.

As already noted in the experimental results of experiments HGR-12, 13, and 14, the ratio of catalyst deactivation increased as the fresh gas feed rate increased. It is possible that higher rates of carbon deposition and metal sintering occur at the higher feed rates to result in higher deactivation rates.

In comparing catalyst performance in an adiabatic hot gas recycle reactor vs an isothermal tube-wall reactor, the catalyst in the tube-wall reactor in experiment TWR-6 deactivated much slower than did the catalyst in the best gas recycle test, HGR-14, (0.009 vs 0.0291 per cent/mscf/lb) and produced much more methane per pound of catalyst (177 mscf/lb vs 32 mscf/lb). This indicates that adiabatic operation of a methanation catalyst between 300 and 400° C is not as efficient as operating isothermally at a higher temperature level of about 400° C.

Another factor that may account for the relatively higher rate of deactivation for the hot gas recycle reactor system is the entrainment of oil vapors from the hot recycle gas compressor into the catalyst bed. Evidence of this occurrence was shown by traces of heavy oil collected downstream of the hot gas recycle reactor. Such oil vapors would tend to decompose thermally and subsequently foul the catalyst surface with carbon. In future hot gas recycle tests, efforts will be made to eliminate the deposition of oil on the catalyst bed.

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TABLE 1. - Catalyst bed data from hot gas recycle reactor tests

Experiment Nos.	10	12	13	14
Type catalyst.....	Flame-sprayed Raney nickel	Flame-sprayed Raney nickel	Supported nickel	Flame-sprayed Raney nickel
Wt pct nickel.....	42 70	42 70	25	42
Pct activated.....	b/ 1/4	a/ 1/4	100% reduced	70
Plate thickness,inches	.224	.224	--	.046
Space between bare plates,-in.	.006	.006	--	.135
Av. bond coat thickness,inches	.026	.022	(1/4" x 1/4" cylindrical pellets)	.006
Av. catalyst thickness, inches	3.07 x 60	3.07 x 60	3.07 x 24	.022
Bed diameter x length, inches	.257	.257	.103	3.07 x 24
Bed volume,ft ³				.103
Weight of unactivated catalyst.....lb	3.72	2.86	6.80	3.84
Superficial area of cat., ft ²	12.7	12.7	18.6	11.4
Void fraction,.....	0.421	0.436	0.370	0.515

a/ Before leaching

b/ Leaching of aluminum stopped when 70% of the theoretical amount of hydrogen had evolved.

TABLE 2. - Operating data from selected periods in Experiment HGR-10

Period number.....	5	15	26
Hours on stream	168	527	887
Fresh gas:			
Rate.....scfh	200	204	204
H ₂vol pct	75.3	75.3	75.6
COvol pct	24.3	24.6	24.2
CO ₂vol pct	0.2	0.1	0.1
N ₂vol pct	0.0	0.0	0.0
CH ₄vol pct	0.2	0.1	0.2
H ₂ Ovol pct	0.0	0.0	0.0
H ₂ /CO.....	3.10	3.06	3.09
Exposure vel..... scfh/ft ²	15.7	16.0	16.1
Space vel..... hr ⁻¹	779	795	796
Mixed feed gas (wet):			
Rate.....scfh	9138	3744	2401
H ₂vol pct	6.0	13.2	17.7
COvol pct	1.2	2.9	4.3
CO ₂vol pct	1.3	0.7	0.8
N ₂vol pct	0.6	1.4	1.7
CH ₄vol pct	83.1	76.7	71.4
H ₂ Ovol pct	7.8	5.0	4.1
H ₂ /CO	5.06	4.61	4.08
Inlet superficial vel.... f/s	5.44	2.18	1.44
Inlet Reynolds No.	5,000	1,960	1,180
Exposure vel.....scfh/ft ²	51.9	47.5	41.6
Space vel.....hr ⁻¹	35,600	14,600	9,360
Vol. total recycle/vol. fresh gas	44.7	17.4	10.8
Vol. cold recycle/vol. fresh gas	3.1	2.99	3.05

continued:

TABLE 2. Operating data from selected periods in Experiment HGR-10

Period number.....	5	15	26
Temperatures:			
Gas inlet.....° C	370	355	375
Maximum catalyst.....° C	400	425	475
Pressure.....psig	300	300	300
Product gas (wet):			
Rate.....scfh	48.8	55.5	58.3
H ₂vol pct	4.4	9.6	12.1
CO.....vol pct	.7	1.6	2.4
CO ₂vol pct	1.3	.8	.2
N ₂vol pct	.7	1.5	1.8
CH ₄vol pct	84.3	80.0	76.6
H ₂ O.....vol pct	8.6	6.4	6.3
H ₂ /CO.....	6.2	6.0	5.05
Conversion:			
H ₂pct fresh feed	98.6	96.5	95.4
CO.....pct fresh feed	99.3	98.2	97.2
(H ₂ + CO).....pct fresh feed	98.7	96.9	95.9
H ₂pct mixed feed	27.0	29.9	34.6
CO.....pct mixed feed	44.4	45.8	46.5
(H ₂ + CO).....pct mixed feed	29.8	32.7	37.0
Usage ratio.....	3.07	3.01	3.07
Heating valueBtu/scf	952	908	878
Carbon recovery.....pct	87	91	90

TABLE 3. - Operating data from selected periods in Experiment HGR-12

Period number.....	7	20	31	52	55	56
Hours on stream.....	200	539	803	1307	1379	1403
Fresh gas:						
Rate.....scfh	388	383	206	386	386	393
H ₂vol pct	75.5	75.1	75.1	75.6	75.2	75.3
CO.....vol pct	24.4	24.7	24.7	24.4	24.7	24.6
CO ₂vol pct	0.1	0.1	0.1	0	0.1	0
N ₂vol pct	0	0	0	0	0	0
CH ₄vol pct	0	0.1	0.1	0	0	0.1
H ₂ O.....vol pct	0	0	0	0	0	0
H ₂ /CO.....	3.09	3.04	3.04	3.10	3.04	3.06
Exposure vel.....scfh/ft ²	30.6	30.1	16.2	30.4	30.4	30.9
Space vel.....hr ⁻¹	1510	1490	804	1500	1500	1530
Mixed feed gas (wet):						
Rate.....scfh	7380	3450	5820	7760	9670	15,100
H ₂vol pct	14.4	20.2	14.9	20.7	22.3	21.9
CO.....vol pct	2.0	4.2	1.6	4.4	4.2	3.8
CO ₂vol pct	0.5	0.4	0.3	0.6	0.8	1.5
N ₂vol pct	1.3	0.8	1.2	0.3	0.6	0.8
CH ₄vol pct	76.4	70.7	76.6	72.6	66.8	60.8
H ₂ O.....vol pct	5.4	3.7	5.4	1.4	5.3	11.2
H ₂ /CO.....	7.04	4.82	9.20	4.71	5.34	5.70
Inlet superficial vel.....f/s	3.88	1.86	3.41	4.61	5.73	8.93
Inlet Reynolds No.	4,270	1,870	3,060	3,910	4,810	7,510
Exposure vel.....scfh/ft ²	95.6	66.3	75.8	153.0	201.0	306.0
Space vel.....hr ⁻¹	28,800	13,400	22,700	30,200	37,700	58,900
Vol. total recycle/vol. fresh gas	18.0	7.99	27.2	19.1	24.1	37.4
Vol. cold recycle/vol. fresh gas	3.01	2.99	3.04	8.71	3.01	1.20

continued:

TABLE 3. - Operating data from selected periods in Experiment HCR-12

Period Number	7	20	31	52	55	56
Temperatures:						
Gas inlet..... ° C	294	310	360	368	366	365
Maximum catalyst..... ° C	353	422	412	420	422	420
Pressure..... Psig	300	300	300	300	300	300
Product gas (wet):						
Rate..... scfh	94.6	97.6	45.9	98.8	105.5	127.7
H ₂ vol pct	10.9	13.0	12.6	17.6	19.9	20.3
CO..... vol pct	0.8	1.6	0.8	3.3	3.3	3.3
CO ₂ vol pct	0.5	0.5	0.3	0.6	0.9	1.5
N ₂ vol pct	1.3	0.8	1.2	0.3	0.6	0.8
CH ₄ vol pct	79.7	77.5	78.8	75.6	69.0	62.2
H ₂ O..... vol pct	6.8	6.6	6.3	2.6	6.3	11.9
H ₂ /CO.....	13.6	8.13	15.8	5.33	6.03	6.15
Conversion:						
H ₂ pct fresh feed	96.5	95.6	96.3	94.0	92.8	91.2
CO..... pct fresh feed	99.2	98.4	99.3	96.5	96.3	95.6
(H ₂ + CO)..... pct fresh feed	97.1	96.3	97.0	94.6	93.6	92.3
H ₂ pct mixed feed	26.6	39.5	17.2	17.1	12.5	8.18
CO..... pct mixed feed	62.3	64.4	53.6	26.6	22.8	16.0
(H ₂ + CO)..... pct mixed feed	31.1	43.8	20.7	18.7	14.1	9.34
Usage ratio.....	3.01	2.95	2.95	3.02	2.93	2.92
Heating value..... Btu/scf	908	892	899	857	828	802
Carbon recovery..... pct	80	81	72	83	81	87

TABLE 4. - Operating data from selected periods in Experiment HGR-13

Period number.....	6	20	22	34	37	50	54
Hours on stream	168	504	552	840	912	1224	1320
Fresh gas:							
Rate.....scfh	211	216	310	320	211	205	210
H ₂ vol pct	75.3	76.4	75.5	74.9	74.9	76.1	75.8
CO..... vol pct	24.6	23.6	24.5	24.9	24.9	23.7	24.1
CO ₂ vol pct	0	0	0	0.1	0.1	0.1	0.1
N ₂ vol pct	0	0	0	0	0	0	0
CH ₄ vol pct	0.1	0	0	0.1	0.1	0.1	0
H ₂ O..... vol pct	0	0	0	0	0	0	0
H ₂ /CO	3.06	3.24	3.08	3.01	3.01	3.21	3.15
Exposure vel.. .scfh/ft ²	11.3	11.6	16.7	17.2	11.3	11.0	11.3
Space vel.. .hr ⁻¹	2050	2110	3020	3120	2060	2000	2050
Mixed feed gas (wet):							
Rate.....scfh	2260	2090	3400	3430	2040	2800	3010
H ₂ vol pct	15.2	16.1	16.9	19.1	15.2	17.9	14.0
CO..... vol pct	2.3	2.5	2.6	3.4	2.9	2.3	2.5
CO ₂ vol pct	0.2	0.3	0.6	0.7	0.6	0.7	0.4
N ₂ vol pct	0.9	1.4	1.0	0.9	0.9	0.5	1.2
CH ₄ vol pct	76.9	75.6	74.5	71.9	76.7	66.8	81.0
H ₂ O..... vol pct	4.5	4.1	4.4	4.0	3.7	11.8	0.9
H ₂ /CO	6.54	6.43	6.41	5.69	5.21	7.72	5.69
Inlet superficial vel.. .f/s	1.20	1.11	1.81	1.82	1.09	1.49	1.60
Inlet Reynolds No.	835	772	1240	1220	753	1010	1120
Exposure vel.. .scfh/ft ²	21.3	21.0	35.8	41.5	19.9	30.5	26.6
Space vel.. .hr ⁻¹	22,000	20,400	33,100	33,400	19,900	27,300	29,400
Vol. total recycle/vol. fresh gas	9.73	8.68	9.98	9.73	8.68	12.7	13.3
Vol. cold recycle/vol. fresh gas	2.98	2.99	3.00	2.96	2.98	1.01	9.05

continued:

TABLE 4. - Operating data from selected periods in Experiment HGR-13

Period number	6	20	22	34	37	50	54
Temperatures:							
Gas inlet..... ° C	301	300	301	301	302	301	301
Maximum catalyst..... ° C	401	400	401	400	401	401	400
Pressurepsig	300	300	300	300	300	300	300
Product gas (wet):							
Rate.....scfh	48.1	50.9	79.3	81.1	49.0	47.4	38.4
H ₂vol pct	8.8	9.0	10.8	13.1	8.2	13.1	9.2
CO.....vol pct	0	0.1	0.4	1.1	0.4	0.6	0.8
CO ₂vol pct	0.3	0.3	0.7	0.8	0.6	0.8	0.4
N ₂vol pct	0.9	1.5	1.0	0.9	1.0	0.5	1.3
CH ₄vol pct	83.0	82.2	80.3	77.8	83.6	71.0	85.7
H ₂ O.....vol pct	7.0	6.9	6.8	6.3	6.2	14.0	2.6
H ₂ /CO.....	-	90	27	11.9	20.5	21.8	11.5
Conversion:							
H ₂pct fresh feed	97.3	97.2	96.3	95.6	97.5	96.0	97.8
CO.....pct fresh feed	100	99.9	99.6	98.9	99.6	99.4	99.4
(H ₂ + CO).....pct fresh feed	98.0	97.9	97.1	96.4	98.0	96.8	98.2
H ₂pct mixed feed	45.0	47.2	39.1	34.9	49.6	29.9	37.0
CO.....pct mixed feed	100	96.2	85.3	68.2	87.9	74.4	68.0
(H ₂ + CO).....pct mixed feed	52.3	53.8	45.3	39.8	55.7	35.0	41.6
Usage ratio.....	2.71	2.95	2.73	2.91	2.94	3.10	3.09
Heating value.....Btu/scf							
Heating value.....	935	926	911	890	933	888	925
Carbon recovery.....pct							
Carbon recovery.....	82	87	90	80	78	70	63

TABLE 5. - Experiment HGR 14 - Selected Test Data

Period number.....	4	15	17	26	34	37	62	64	76
Hours on stream.....	139	462	534	750	1058	1130	1732	1803	2091
Fresh Gas:									
Rate.....scfh	207	214	306	307	207	207	210	203.5	213
H ₂vol pct	75.8	75.4	75.3	74.6	75.1	75.1	75.4	74.7	75.4
CO.....vol pct	23.7	23.6	23.6	24.4	22.9	23.6	24.0	24.8	24.1
CO ₂vol pct	0.1	0.1	0.3	0.2	0.1	0.1	0.1	0.1	0.1
N ₂vol pct	0.4	0.9	0.7	0.8	1.8	0.8	0.8	0.3	0.4
CH ₄vol pct	0	0	0.1	0	0.1	0.1	0	0.1	0
H ₂ O.....vol pct	0	0	0	0	0	0	0	0	0
H ₂ /CO.....	3.20	3.19	3.19	3.06	3.28	3.19	3.13	3.01	3.13
Exposure vel..... scfh/ft ²	18.0	18.6	26.5	26.6	17.8	17.9	18.2	17.7	18.6
Space vel..... hr ⁻¹	2010	2090	2980	2990	2020	2020	2050	1980	2080
Mixed feed gas (wet):									
Rate.....scfh	2360	2400	3710	3720	2240	2430	2760	2120	2430
H ₂vol pct	15.9	14.0	11.7	8.8	11.8	11.1	10.1	10.4	13.8
CO.....vol pct	2.1	2.1	2.0	2.2	2.2	2.2	2.1	2.9	2.9
CO ₂vol pct	0.1	0.1	0.2	1.5	0.2	0.4	0.7	0.4	0.7
N ₂vol pct	0.7	1.1	0.9	1.1	1.3	0.9	1.1	1.1	1.2
CH ₄vol pct	76.4	78.0	80.6	81.9	84.3	80.7	81.4	85.2	76.9
H ₂ O.....vol pct	4.8	4.6	4.6	4.5	0.2	4.7	4.6	0	4.5
H ₂ /CO.....	7.68	6.63	5.88	4.00	5.38	5.10	4.84	3.64	4.77
Inlet superficial vel....f/s	1.25	1.27	1.97	1.97	1.19	1.29	1.46	1.12	1.29
Inlet Reynolds No.....	546	563	882	898	532	582	666	512	570
Exposure vel.....scfh/ft ²	37.2	34.0	44.5	35.8	27.5	28.2	29.6	24.8	35.6
Space vel.....hr ⁻¹	23,000	23,400	36,100	36,200	21,800	23,700	26,900	20,700	23,700
Vol. total recycle/vol.fresh gas	10.7	10.4	11.3	11.3	10.1	11.0	12.4	9.66	10.6
Vol. cold recycle/vol.fresh gas	2.95	2.93	3.12	3.01	9.59	2.93	3.13	10.2	2.94

continued:

TABLE 5. - Experiment HGR 14 - Selected Test Data

Period number.....	4	15	17	26	34	37	62	64	76
Temperatures:									
Gas inlet.....° C	299	299	301	300	300	300	300	299	299
Maximum catalyst.....° C	400	400	400	400	401	400	395	397	398
Pressure.....psig	300	300	300	300	300	300	300	300	300
Product gas (wet):									
Rate.....scfh	32.9	28.4	44.2	45.4	27.3	27.6	43.9	44.7	40.6
H ₂vol pct	10.0	7.9	5.8	2.8	5.3	5.0	4.7	3.5	7.8
CO.....vol pct	0	0	0.1	0.2	0.1	0.2	0.3	0.5	0.9
CO ₂vol pct	0.1	0.1	0.2	1.6	0.2	0.5	0.7	0.5	0.7
N ₂vol pct	0.7	1.1	0.9	1.1	1.2	0.9	1.1	1.2	1.3
CH ₄vol pct	81.9	83.9	86.1	87.6	90.7	86.3	86.5	91.8	82.5
H ₂ O.....vol pct	7.3	7.0	6.9	6.7	2.5	7.1	6.7	2.5	6.8
H ₂ /CO.....	-	785	117	14.1	58.3	27.7	16.2	6.68	9.14
Conversion:									
H ₂pct fresh feed	97.9	98.6	98.9	99.4	99.1	99.1	98.7	99.0	97.9
CO.....pct fresh feed	100	100	100	99.9	99.9	99.9	99.7	99.5	99.2
(H ₂ + CO).....pct fresh feed	98.4	98.9	99.1	99.5	99.3	99.3	98.9	99.1	98.2
H ₂pct mixed feed	40.4	47.0	52.2	69.5	57.7	57.0	55.4	67.8	46.5
CO.....pct mixed feed	100	99.6	97.8	91.5	96.2	92.2	86.8	82.6	72.1
(H ₂ + CO).....pct mixed feed	47.3	53.9	58.9	73.9	63.7	62.7	60.8	71.0	50.9
Usage ratio.....	3.10	3.13	3.14	3.04	3.23	3.15	3.09	2.99	3.08
Heating value.....Btu/scf	930	941	957	962	961	960	956	967	927
Carbon recovery.....pct	83.1	74.2	79.0	78.5	94.5	98.3	94.4	89.4	86.5

TABLE 6. IRON AND CARBON CONTENT OF RANEY NICKEL CATALYST GRIDS
AFTER EXPERIMENT HGR-10

GRID	Weight Percent	
	Fe	C
A ^{1/}	22.0	13.4
B	17.2	9.1
C	3.5	3.9
D	2.7	3.3
E	2.0	2.5
F	2.1	2.0
G	.9	1.5
H	.8	1.6
I	.8	1.6
TOP ^{2/}	.8	1.9

^{1/} GAS IN

^{2/} GAS OUT

TABLE 7. SURFACE AREAS, PORE VOLUMES, AND PORE RADII
OF SPENT RANEY NICKEL CATALYST

EXPERIMENT HGR-12

DISTANCE FROM GAS INLET, INCHES	B.E.T. SURFACE AREA, m^2/gm	AV. PORE RADIUS, Å	PORE VOL. cm^3	PERCENT PORE VOLUME WITH THE FOLLOWING RADII				
				< 30Å	30-40Å	40-50Å	50-60Å	> 60Å
0	34.7	47.1	0.083	19.7	11.9	10.8	10.0	47.6
18	31.7	90.6	.146	8.8	6.2	4.9	6.4	73.6
30	34.4	58.6	.101	15.7	9.2	11.6	9.5	54.0
36	32.9	82.0	.135	10.4	7.4	8.0	6.0	68.2
48	24.2	139.0	.168	.5	3.7	7.5	4.7	83.6
60	19.5	109.5	.107	0	0	0	4	96.0

TABLE 8. - Properties of spent methanation catalysts

	Exp. HGR-12		Exp. HGR-13		Exp. HGR-14	
	Catalyst		Catalyst		Catalyst	
	At Inlet	At Outlet	At Inlet	At Outlet	At Inlet	At Outlet
X-Ray analysis	-	-	Ni	Ni	Ni, Ni ₃ C	Ni
Chemical analysis, per cent:						
Ni	67.6	80.4	24.0	25.3	83.4	81.9
Al	13.1	9.6	-	-	6.23	7.90
C	1.74	0.8	5.1	5.2	3.53	0.81
Fe	0.35	0.45	0.12	0.20	1.18	1.21
Na	0.08	0.06	0.23	0.20	-	-
S	0.24	0.13	0.1	0.1	0.19	0.07
Surface area (B.E.T.), m ² /gm	34.67	19.50	-	-	30.95	29.7
Metal surface area (chemisorbed hydrogen), m ² /gm	1.3	4.9	-	-	-	-
Average pore radius, Å	47.07	109.53	-	-	48.01	56.69
Percent pore volume > 60Å ⁰	47.56	95.97	-	-	42.3	64.2

TABLE 9. - Effect of cold recycle upon product gas

Exp. No.	Stream time, hours	Cold recycle ratio	H ₂ O in mixed feed, %	Product gas analysis, per cent, wet basis				Apparent mass action constants, k _p		Max temp, °C	
				H ₂ O	H ₂	CO	CO ₂	CH ₄	shift reaction		methanation reaction
HGR-12	1307	8.7:1	1.4	2.6	17.6	3.3	0.6	75.6	.78	.24	420
HGR-12	1379	3.0:1	5.3	6.3	19.9	3.3	0.9	69.0	.86	.37	422
HGR-12	1403	1.2:1	11.2	11.9	20.3	3.3	1.5	62.2	1.2	.59	420
HGR-12	539	3.0:1	5.4	6.6	13.0	1.6	0.5	77.5	1.6	3.2	422
HGR-13	1224	1.0:1	11.8	14.0	13.1	0.6	0.8	71.0	.79	16.0	401
HGR-13	1320	9.1:1	0.9	2.6	9.2	0.8	0.4	85.7	.57	7.8	400
HGR-14	462	2.9:1	4.6	7.0	7.9	0.01	0.1	83.9	.075	2650	400
HGR-14	2091	3.0:1	4.5	6.8	7.8	0.9	0.7	82.5	1.02	30.8	398
HGR-14	2307	1.0:1	10.5	13.2	10.1	0.8	1.4	73.0	.75	25.3	398

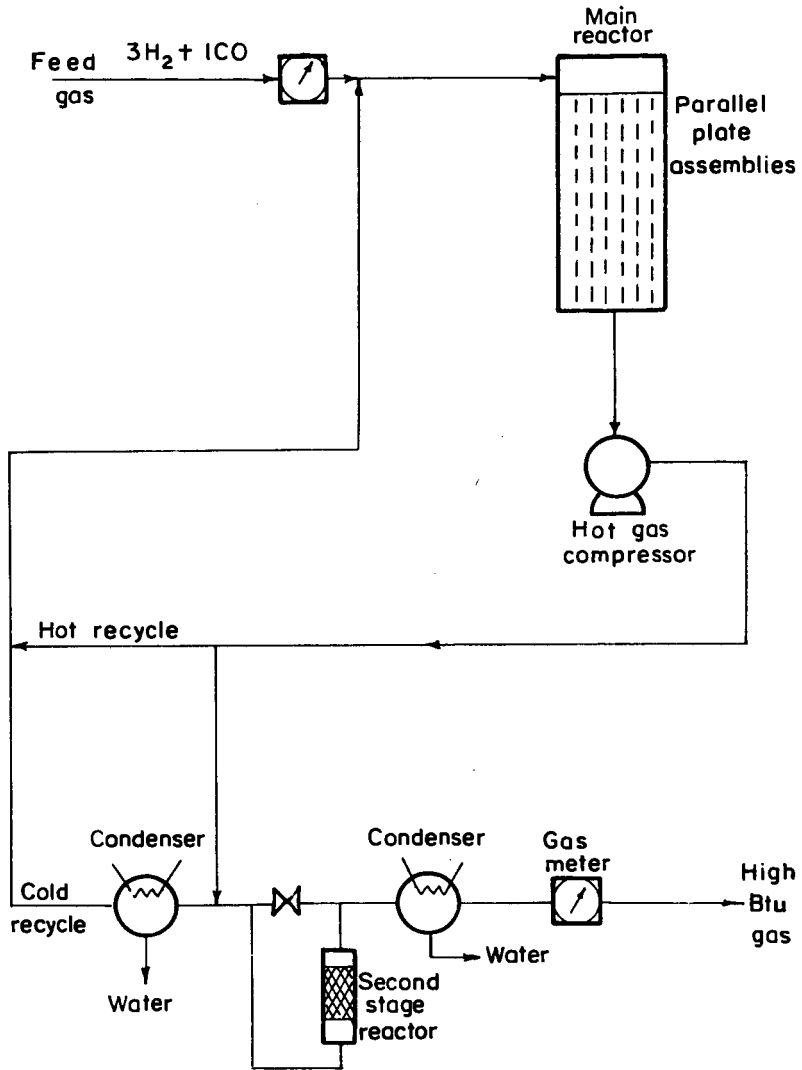


Figure 1 — Flowsheet of hot-gas recycle process

L-13681

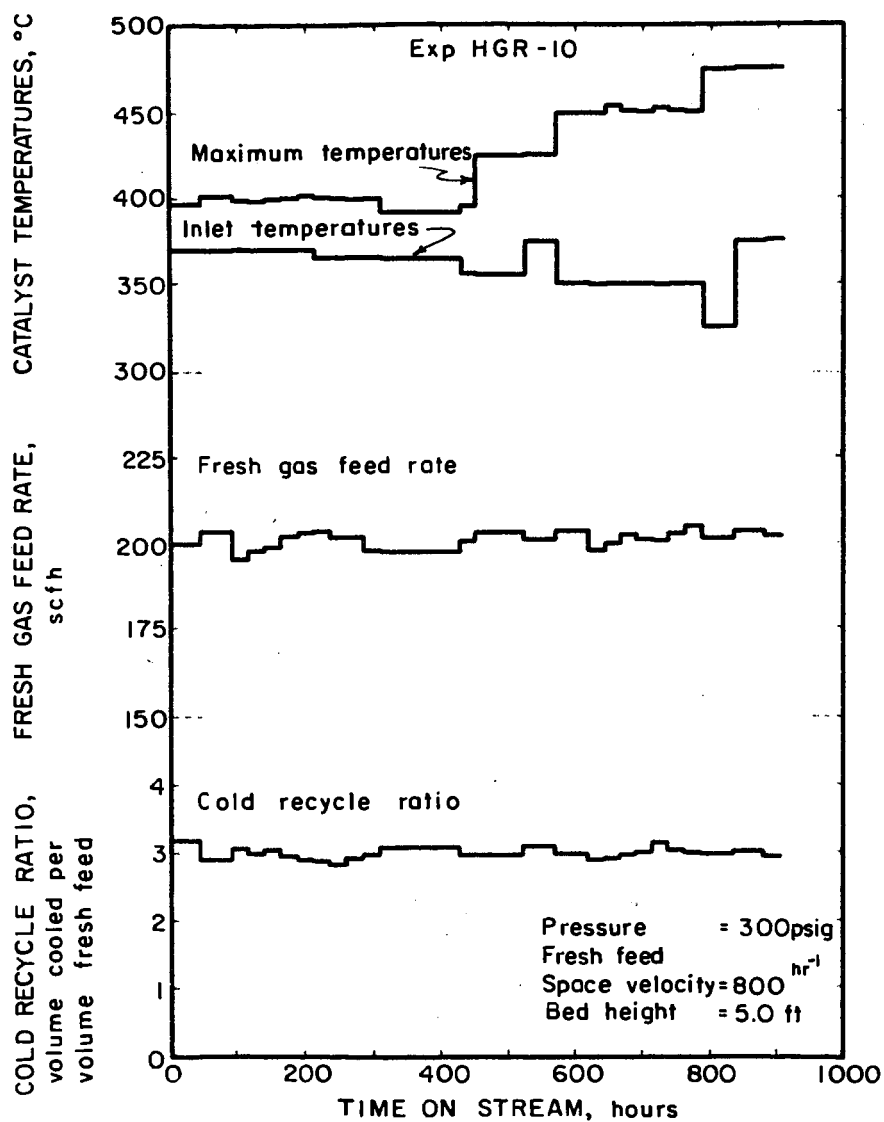


Figure 2 — Reactor conditions.

L-13676

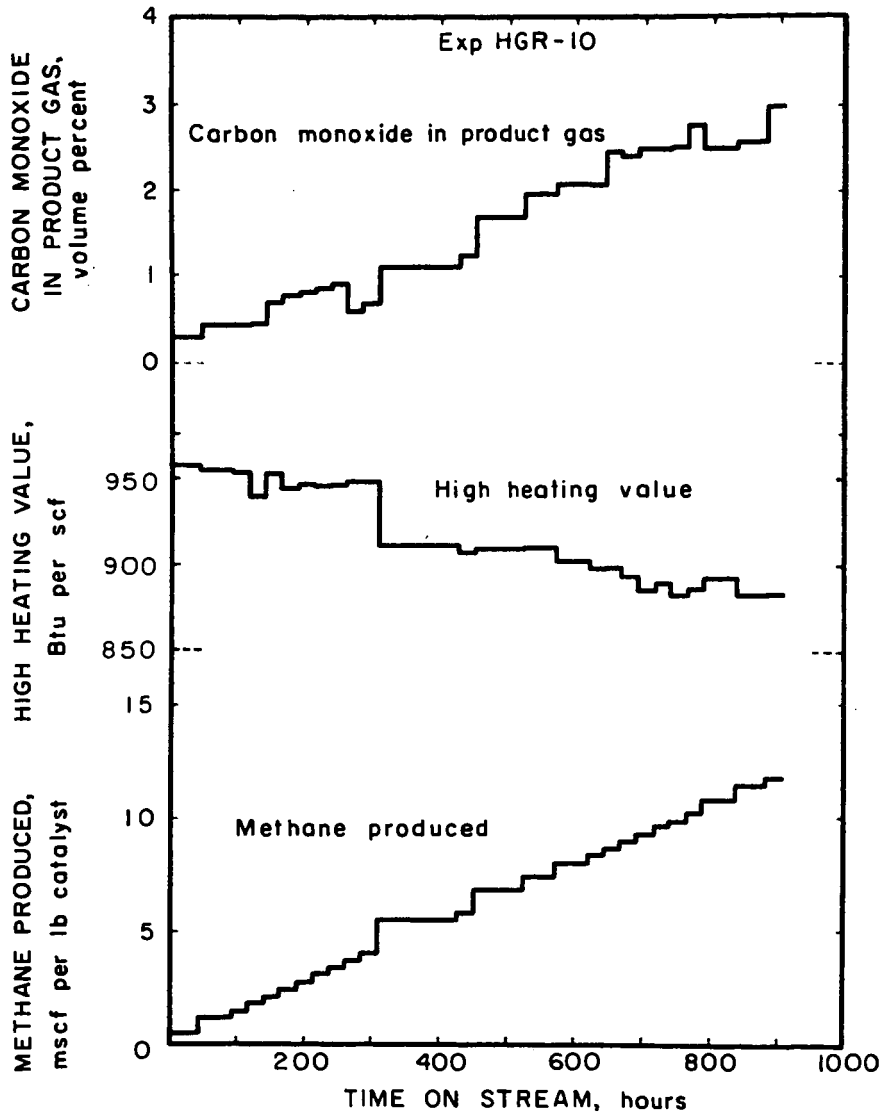


Figure 3—Product gas characteristics

L-13673

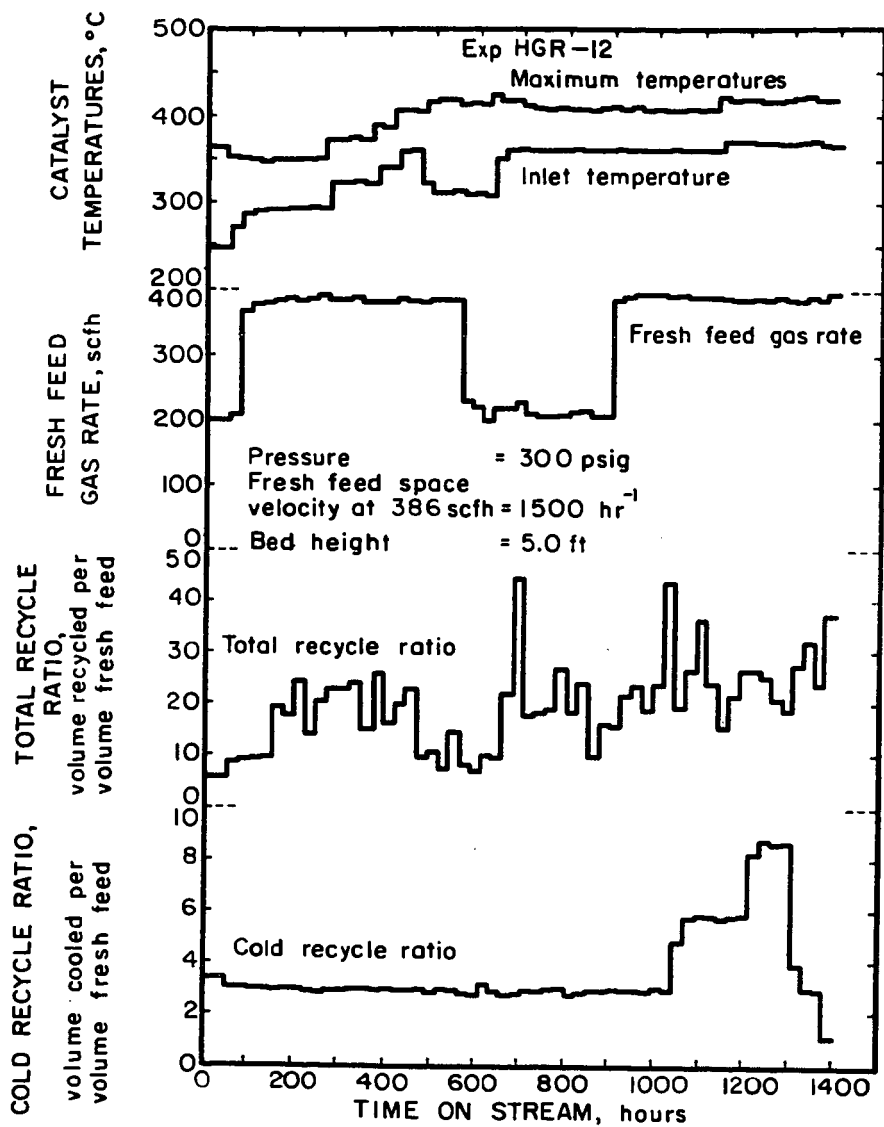


Figure 4 - Reactor conditions

L-13678

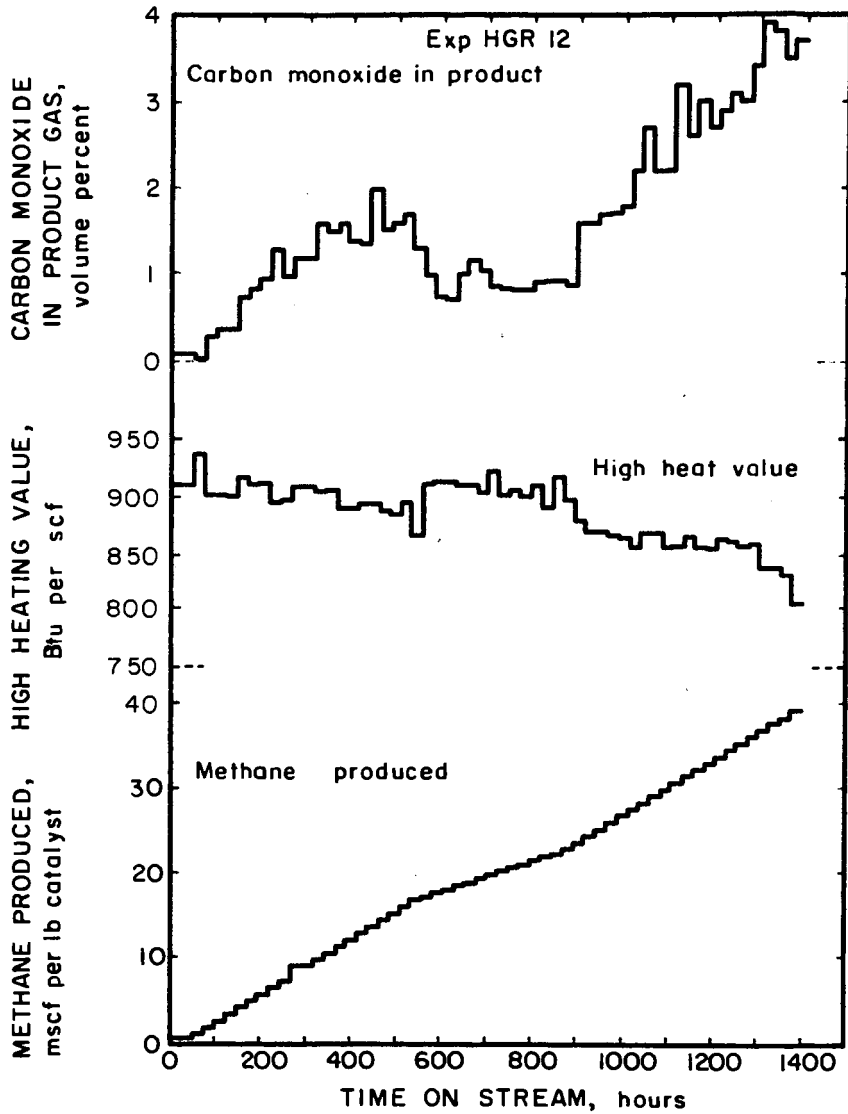


Figure 5 - Product gas characteristics

L-13674

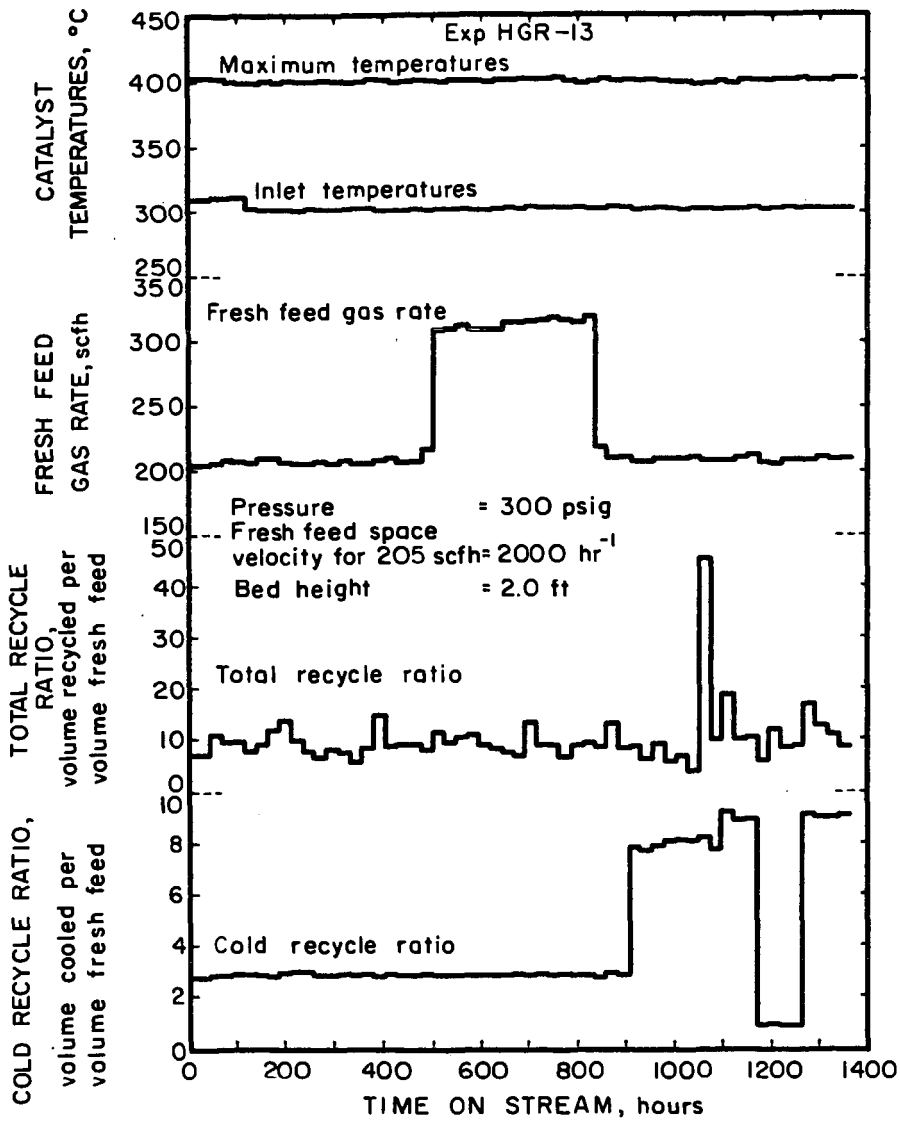


Figure 6 - Reactor conditions

L-13677

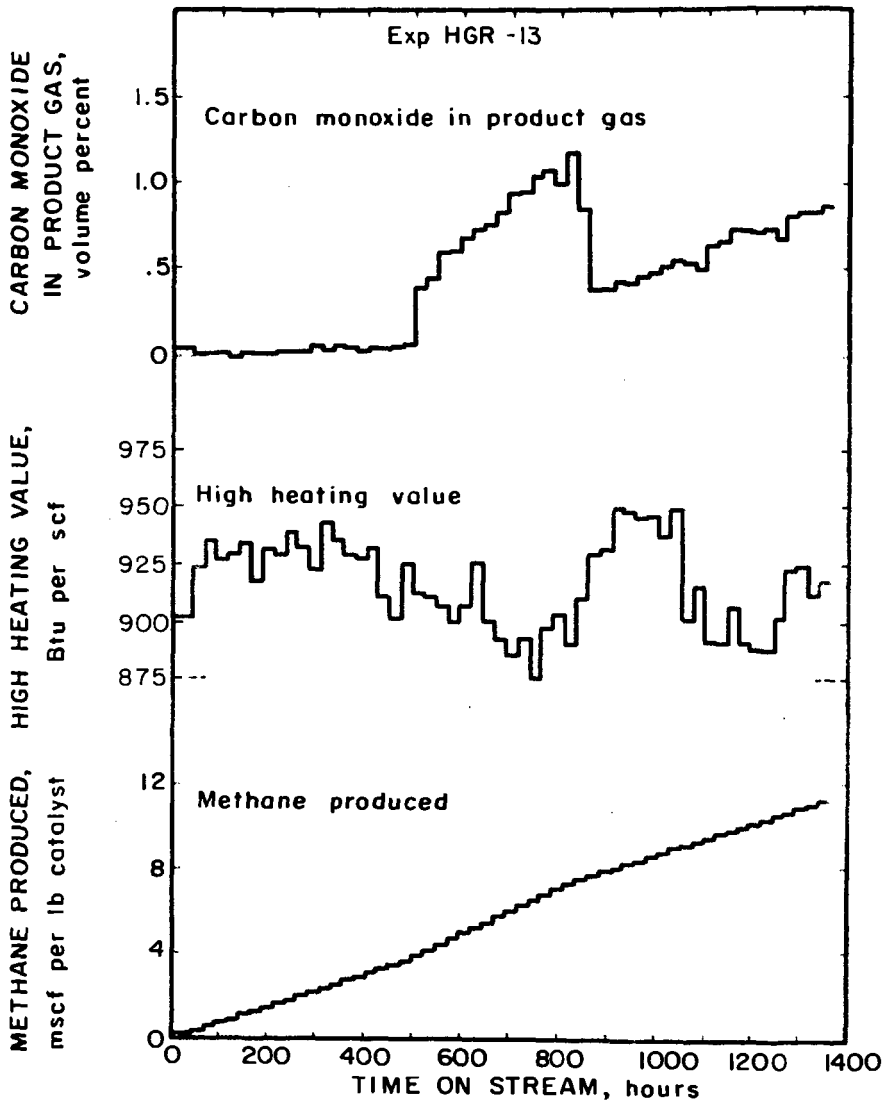


Figure 7 — Product gas characteristics

L-13675

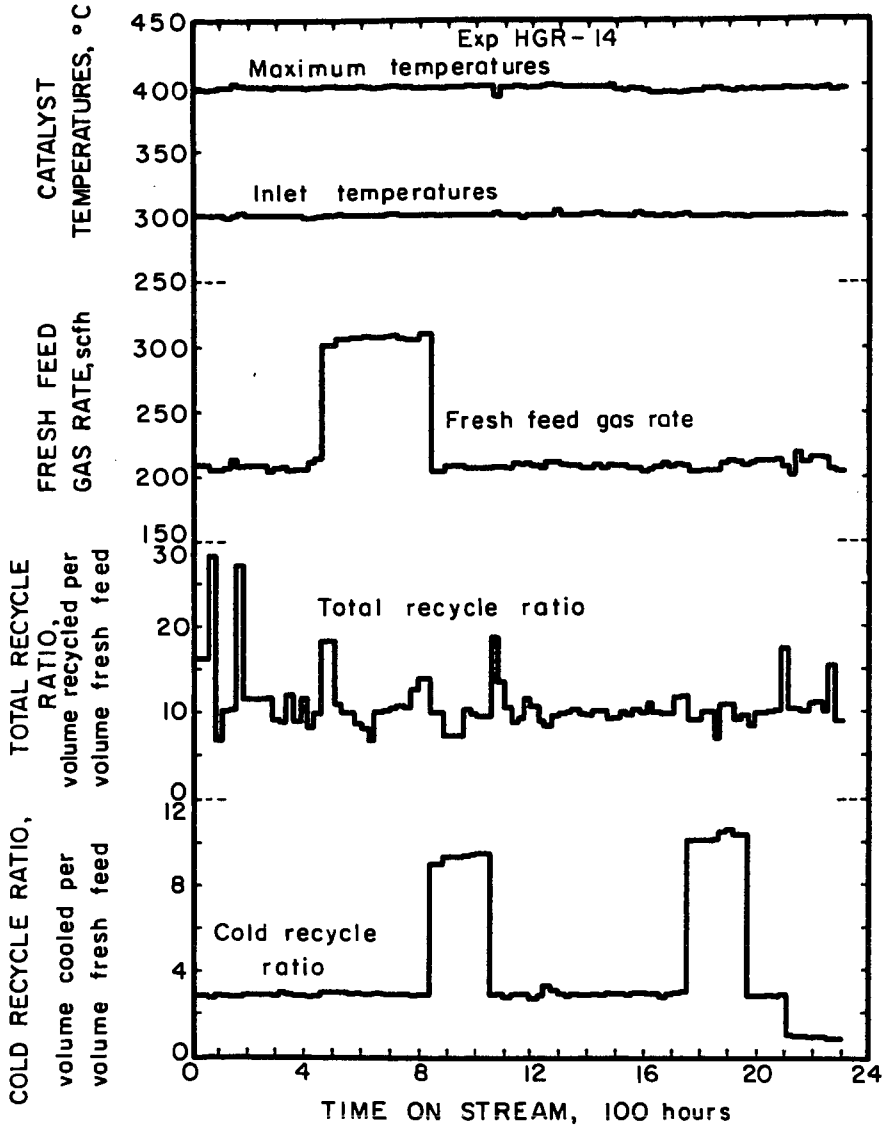


Figure 8 — Reactor conditions

L-13680

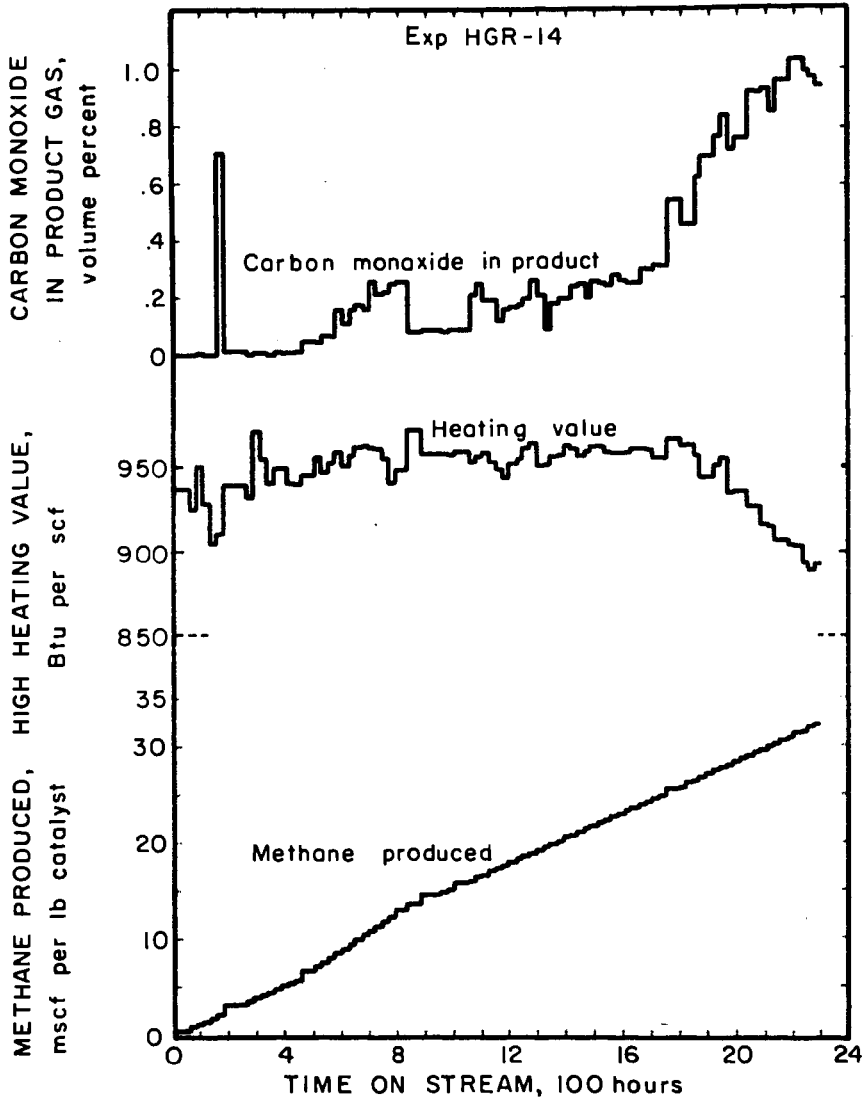


Figure 9 — Product gas characteristics

L-13679

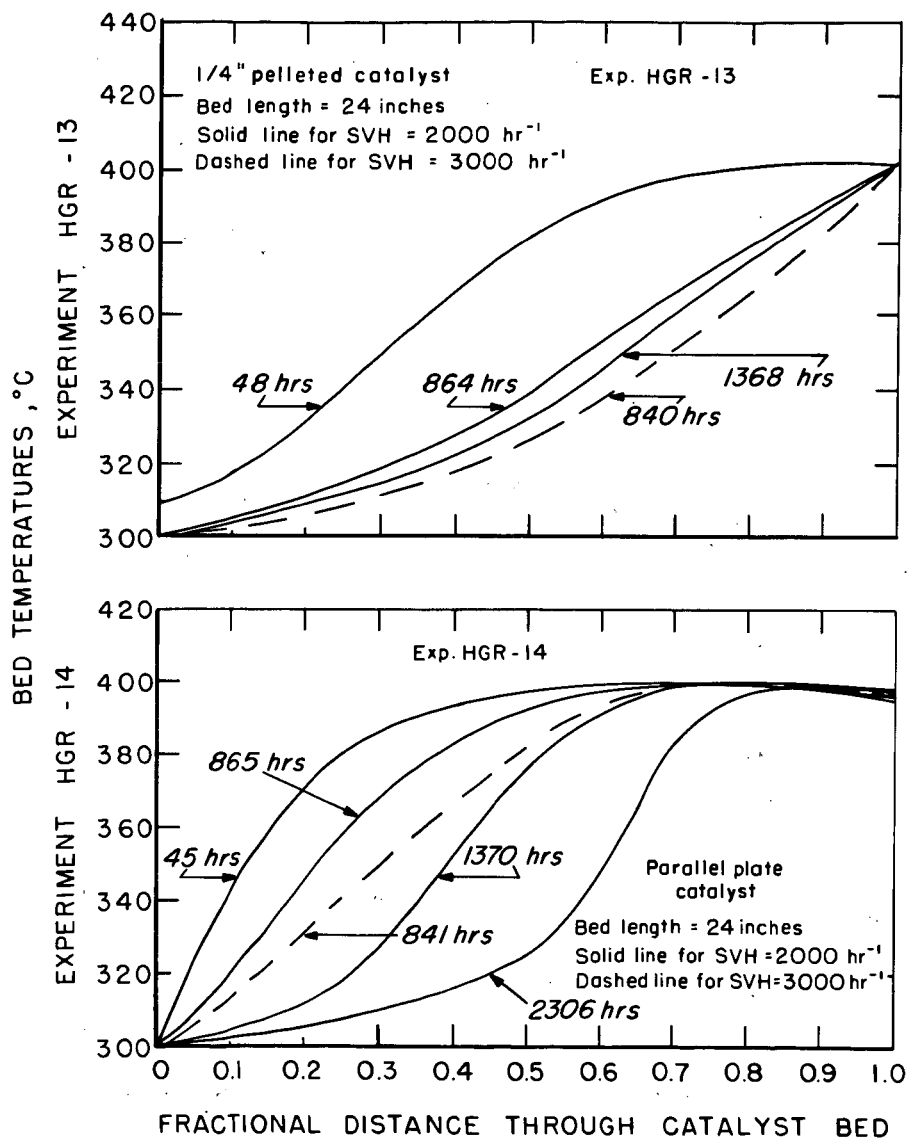


FIGURE 10-Axial temperature profiles, methanation Exp. HGR 13 and 14.

OPERATING EXPERIENCE WITH THE METHANATION UNITS IN THE HYGAS
PILOT PLANT, W. G. Bair, Institute of Gas Technology, 4201 West 36th Street,
Chicago, Illinois 60632

The HYGAS process includes a methanation section utilizing a fixed bed catalyst, multiple reactor stages and cold, product gas recycle for temperature control. To date about 550 hours of operation have been obtained on this unit with a wide range of H_2/CO ratio feed gases. Complete conversion (less than 10 ppm in the product gas) of CO has been obtained in all operation to date.

This paper describes the equipment, process controls, catalyst, and instrumentation of the system and gives operating conditions and results.

LIQUID PHASE METHANATION OF HIGH CONCENTRATION CO SYNTHESIS GAS

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Dr. David B. Blum
Dr. Martin B. Sherwin
Mr. Marshall E. Frank

American Chemical Society
Division of Fuel Chemistry
Atlantic City, New Jersey
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I INTRODUCTION

Development work on the Liquid Phase Methanation process commenced on April 25, 1972 and was first reviewed in October, 1972 at the 4th Annual Pipeline Gas Symposium. The development has proceeded in a very successful manner. Prior to reviewing these recent accomplishments, the basic Process and Program background will be briefly reviewed for those attendees who are not familiar with the technology.

A. Process Background

The Liquid Phase Methanation Process is ideally suited to the safe and reliable conversion of high concentration carbon monoxide streams to methane. The exothermic heat of reaction, which under adiabatic conditions could theoretically cause temperature rises of about 1700°F in a non-recycle situation is easily removed by the inert fluidizing liquid in a near isothermal system. This is achievable by effecting the heterogeneously catalyzed reaction of the feed gases in the presence of an inert liquid phase which absorbs the large exothermic heat of reaction. The reaction proceeds to near completion in a single pass and economic studies will dictate whether a single stage reactor will be used or if a polishing reactor should be utilized in the final design.

Figure 1 illustrates the process in more detail. The inert liquid is pumped upflow through the reactor at a velocity sufficient to both fluidize the catalyst and remove the reaction heat. The low BTU feed gas is passed cocurrently up the reactor where it is catalytically converted to a high concentration methane stream. The exothermic reaction heat is taken up by the liquid mainly as sensible heat and partly by vaporization (depending upon the volatility of the liquid). The overhead product gases are condensed to remove the product water and to recover any vaporized liquid for recycle. The main liquid flow is circulated through a heat exchanger where the heat of reaction is removed by generating high pressure steam. This also provides excellent temperature control for the system.

B. Project Background

Development of the Liquid Phase Methanation Process is included within the AGA/OCR joint program on synthetic natural gas production from coal. The development program is divided into three phases which have been proceeding in an overlapping manner. These are reviewed below:

<u>Phase</u>	<u>Object</u>	<u>Percent Completion</u>
I	Exploratory Research and Development	100
II	Construction and Operation of a Larger Scale Process Development Unit (PDU)	90
III	Construction and Operation of a Full Scale Integrated Pilot Plant	40

Completion of the program is scheduled for June 30, 1975.

II DESCRIPTION OF EQUIPMENT

A. Bench Scale

The bench scale reactor is 0.81" I.D. x 48" long. The nominal feed gas rate for this unit is 30 SCFH, and is supplied from premixed high pressure gas cylinders. Except for reaction temperature, the bench scale unit is substantially manually operated and controlled. The catalysts used in these studies were standard commercial methanation catalysts, ground to a 16-20 mesh size, which is compatible with the small reactor diameter.

B. Process Development Unit (PDU)

The nominal feed gas rate for the unit is 1500 SCFH which is a scale-up of 50-100 times the bench scale unit. The methanation reactor is 4" O.D. x 84" high and the catalyst bed height can be varied from 2 to 7 feet. The basic design and flow scheme of the PDU is similar to the bench scale unit. The product gases, following analysis, are sent to an incinerator where they are thermally oxidized to carbon dioxide and water prior to discharge to the atmosphere. Sufficient instrumentation is provided for complete automatic control and monitoring from a remote control room. The reactor is fitted with movable gamma ray detector which is used to measure density differences between the source (radioactive material) and the detector. In this manner we are able to accurately determine the height of the fluidized catalyst bed under varying reaction conditions.

The overall objectives of this phase of the program are:

- Determine effect of all process variables for optimum performance.
- Determine data needed for reliable engineering design and cost estimates of larger plants.
- Determine catalyst life, recovery and regeneration methods.
- Determine liquid life and effectiveness.
- Determine whether reaction model correlation is valid for PDU performance.

C. Pilot Plant

The third phase of the liquid phase methanation project is the design, construction and operation of a large pilot plant. The basic objectives are to demonstrate the process on a synthesis gas actually produced in a coal gasification process and obtain the necessary design and performance data such that detailed design and engineering can be accomplished for a full size (ca. 250 MM SCFD) coal gasification plant. The reactor design in the pilot plant is 2' diameter by 15' long. This we feel is large enough to provide adequate scale-up information for commercial sized reactors. Again, the design is basically the same as for the PDU and bench scale unit, but obviously modified and adapted for the larger capacity. The scheduled start-up of the pilot plant is June, 1975.

The pilot plant will be located at the site of an existing coal gasification process. At this time, the two most logical places are the IGT plant in Chicago or the CO₂ Acceptor plant in Rapid City, South Dakota. The design concept is to build a skid-mounted unit that could be located at either place or at other locations where coal gasification processes are under construction. With a skid-mounted unit, it could be operated at one site for a period of time and then moved to another location for testing with synthesis gas from another coal gasification process.

The design of the unit is such that it can accommodate synthesis gas feed from any one of a number of processes. The unit will be designed to handle a maximum feed gas of 2 MM SCFD at 1100 psig. This is the maximum output of the IGT Hygas plant. The LPM process can also operate at lower pressure and, hence, Rapid City would handle the lower pressure feed gas. The synthesis gas feed there is only 0.6 MM SCFD and is available at 100 psig.

III REACTION CORRELATING MODEL

One of the goals of our experimental program in the bench scale unit was to develop the necessary correlations for use in the ultimate design of large commercial plants. With the complexity inherent in the three phase, gas-liquid-solid reaction systems, many models can be postulated. As a background to how a reaction model was finally selected, the physical situation in the three phase system is briefly reviewed.

1. The gas bubbles, after entering the reactor, rise due to convection and buoyancy. On the other hand, the presence of a solid phase retards the upward bubble motion according to its void spacing and particle size.
2. The reactants are transferred from the gas bubbles to the bulk liquid through the gas-liquid interface. Consideration of the relative resistances shows that the liquid film coefficient at the gas-liquid interface should be the least efficient mass transfer step and that the liquid phase concentration at the gas-liquid interface is governed by Henry's Law.
3. The reactants, after diffusing from the gas-liquid interface to the bulk liquid, are convected by the fluid motion to the liquid-catalyst interface.
4. Mass transfer of the reactants from the bulk liquid across the liquid catalyst interface should again be governed by the liquid film coefficient.
5. After absorbing on the catalyst surface, the reactants undergo a catalytic surface reaction.
6. The reaction products desorb and are transferred back to the gas bubbles according to Steps 4 to 1.

As our first approach to the model we considered the controlling step to be one of the following:

- The mass transfer from gas to liquid.
- The mass transfer from liquid to catalyst.
- The catalytic surface reaction step.

The other steps were eliminated since convective transport with small catalyst particles and high local mixing should offer virtually no resistance to the overall reaction scheme. Mathematical models were constructed for each of these three steps.

Our initial experimental results indicated that the kinetic model — first order in liquid phase CO concentration — was the leading candidate. We designed an experimental program then with this reaction model specifically in mind. The integrated rate expression (1) can be written as:

(1) See Appendix for nomenclature.

$$\ln \left(\frac{1}{1-X_T} \right) = \frac{k(P_T - P^*)}{K_{H_{CO}} (M/p_L) (1-2Y_{CO}^0) F^0} W$$

Therefore a plot of:

$$\ln \left(\frac{1}{1-X_T} \right) \quad \text{as} \quad \frac{(P_T - P^*)}{F^0 (1-2Y_{CO}^0)} W$$

should result in a straight line through the origin, where the slope $k/K_H (M/p_L)$ is a direct measure of the catalyst-liquid pair productivity.

Bench Scale Results

We performed this type of process variable scan for several sets of catalyst-liquid pairs. A representative example is shown in Figure 2. In all cases, the data supported the proposed mechanism. In addition, we examined the effect of temperature on the kinetic rate constant, and a typical Arrhenius plot is shown in Figure 3. The activation energy calculated for all of the systems run in the bench scale unit fell within 18,000 to 24,000 cal/gm mole.

Data collected (see Figure 4) during these process variable scans indicated that a larger than expected amount of CO_2 was also being formed. Selectivity to CO_2 reached a maximum of 5-10% at about 90-95% CO conversion. At higher conversions, the CO_2 level is reduced either by reverse shift and subsequent methanation of CO , or by direct methanation of CO_2 . This selectivity to CO_2 can be eliminated by cofeeding small amounts of CO_2 (3-5%). Since multiple CO_2 absorbers are required in the commercial SNG plant, one or more could be relocated downstream of the methanation step. This could offer some economic advantages since CO_2 absorption would now occur at higher concentration and pressure and lower total gas flow.

Process Development Unit Results

Work in the PDU largely paralleled the bench scale reactor tests, with one important addition - extensive three-phase fluidization studies. As we have previously mentioned, the PDU is equipped with a traversing gamma ray density detector, capable of measuring the bed density within ± 0.01 specific gravity units. In this manner we were not only able to measure and correlate fluidized bed expansion as a function of liquid and gas velocities and physical properties but we were also able to determine the individual phase volume fractions. The two major findings of this work were (see Figure 5); (1) the absolute values for the gas holdup are 3-4 times greater than the incremental porosity increase due to the gas flow at constant liquid flow, and (2) the gas holdup is essentially independent of liquid velocity for $1.3 U_{mf} < U_L < 2.5 U_{mf}$. In addition, the data for all the catalysts indicated that the maximum gas volume fraction obtainable was on the order of 0.5-0.6.

Reaction studies were carried out in the PDU in order to verify the correlating model developed in the bench scale unit. This provides data applicable to the scale-up design required for the pilot plant, and ultimately, the commercial unit. The initial work in the PDU was performed with particles much larger ($1/8"-3/16"$) than those used in the bench scale unit ($< 1/32"$), and the reaction rates for

these larger particles were about one-third the rates obtained with the smaller size particles (compare Figures 2 and 6). In addition, the activation energy obtained with this data was on the order of 11,000 cal/gm mole; just about one-half the value obtained in the bench unit (compare Figures 3 and 7). These results suggested that we were encountering pore diffusion limitations, and we attempted to verify this result by investigating still smaller particles (1/16"). While the reaction rates increased significantly, as they should, the activation energy remained essentially unchanged, indicating that we were still in the pore diffusion regime. Therefore, we can still further increase productivity by simply reducing particle size. This should not be too difficult since 1/32" particles are already being used in analogous commercial systems. The ultimate productivity obtainable has not yet been accurately defined, although we are confident that a vapor hourly space velocity of 4000 hr⁻¹ at 1000 psig and 650°F with a feed containing 20% CO, 60% H₂, and 20% CH₄ should result in a CO conversion of 95-98%. One should bear in mind that these results do in fact confirm the first order reaction rate model proposed as a result of the earlier bench scale results. Future work will concentrate on the effect of axial dispersion arising from the varying geometries encountered during scale-up and on determining the optimum particle size for the commercial unit.

In an attempt to define useful catalyst life, we have conducted continuous runs of 2 and 4 weeks duration. These results have been encouraging in that after an initial period of deactivation over the first 50-100 hours (common with nickel hydrogenation catalysts), the catalyst reaches an equilibrium productivity in excess of our original design basis of a VHSV equal to 4000 hr⁻¹ at 1000 psig and 650°F. Considering these results, and our substantial experience with all types of catalysts, we have every reason to believe that a catalyst life in excess of one year can be achieved at which point catalyst replacement costs are insignificant on overall SNG economics.

IV CONCLUSIONS

Based on this past work and ongoing experiments, we feel that the Liquid Phase Methanation process promises to become an economic, reliable and versatile means of converting synthesis gas mixtures to high BTU gas. Chem Systems believes this technology to be a key step in the transformation of fossil feeds to pipeline gas and we look forward to its successful application in commercial coal gasification plants.

e_G	= Gas Phase Volume Fraction
e_L	= Bed Porosity; Liquid Only Fluidizing
e_{LG}	= Bed Porosity; Liquid and Gas Fluidizing
F	= Gas Flow Rate at any Position; g moles/sec
k	= Reaction Rate Constant; g moles/sec-gm catalyst-(g mole/cm ³)
K_H	= Henry's Law Coefficient; atm/mole fraction
M	= Liquid Phase Molecular Weight; gm/g mole
ρ_L	= Liquid Phase Density; gm/cm ³
P_T	= Total Pressure; atm
P^*	= Liquid Phase Vapor Pressure; atm
T	= Temperature, °K
U_{mf}	= Minimum Fluidization Velocity; cm/sec
U_{OG}	= Superficial Gas Velocity at Reactor T and P_T ; cm/sec
W	= Weight of Catalyst; gms
X_T	= Fraction of CO Converted

Super Script

0 = Initial Condition

FIGURE 1

LIQUID PHASE METHANATION PROCESS SCHEMATIC

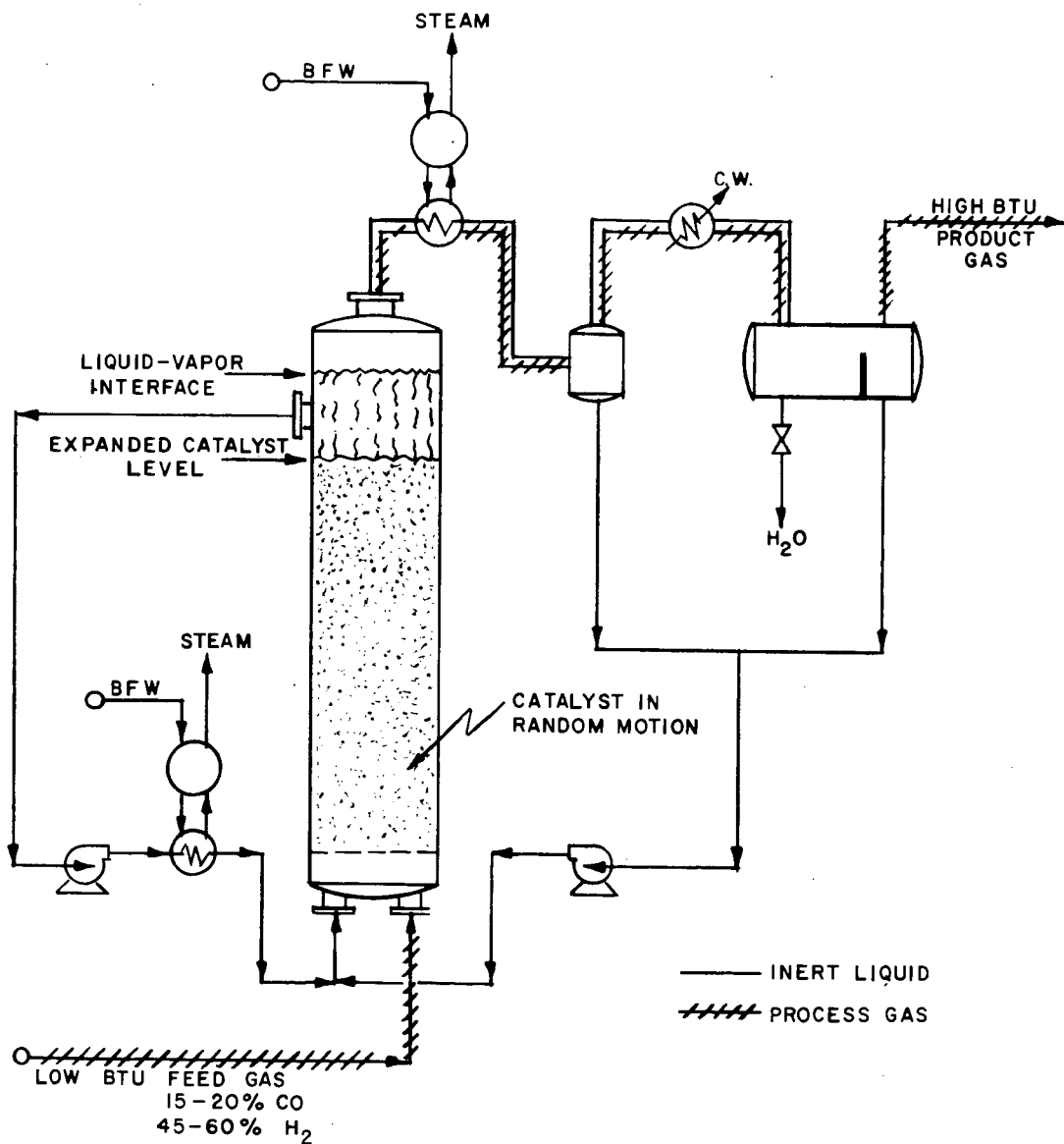


FIGURE 2

CONVERSION VS CONTACT TIME — BENCH SCALE UNIT

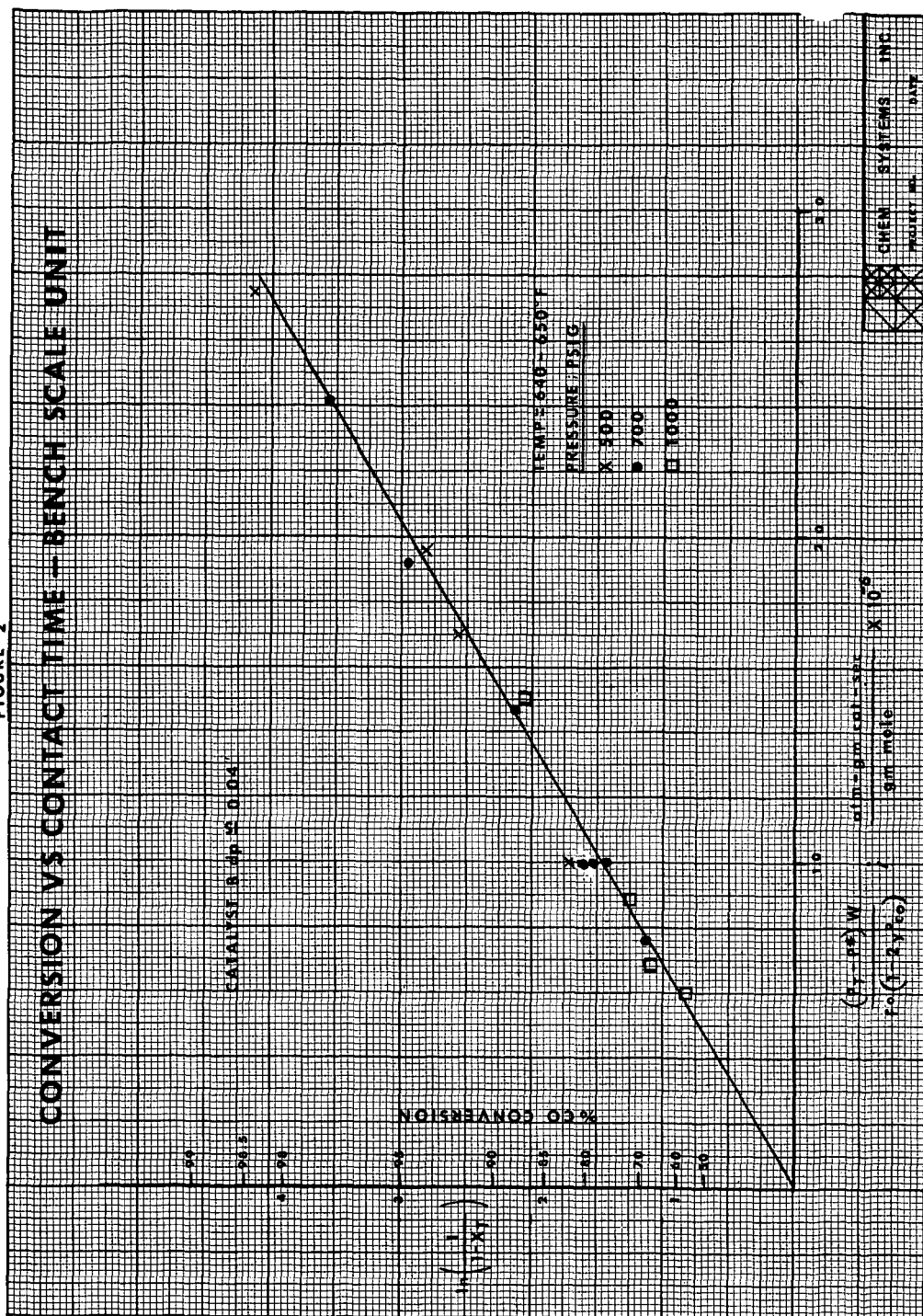


FIGURE 3

TEMPERATURE EFFECT ON KINETIC RATE CONSTANT BENCH SCALE UNIT

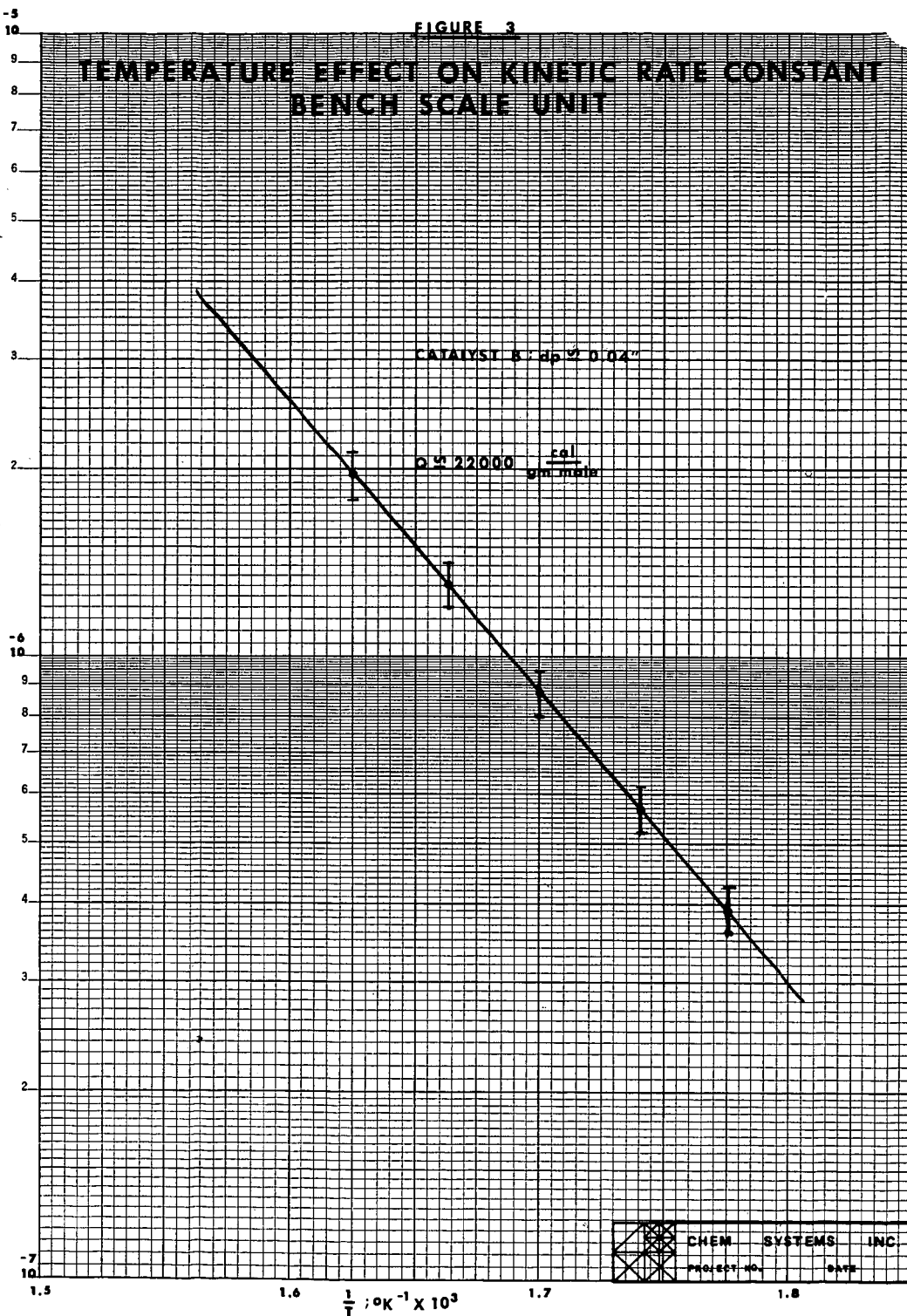
$$\frac{K}{K_H (M/R)} \cdot \frac{\text{gm mole}}{\text{atm-gm cat-sec}}$$


FIGURE 4

CO₂ SELECTIVITY VS CO CONVERSION

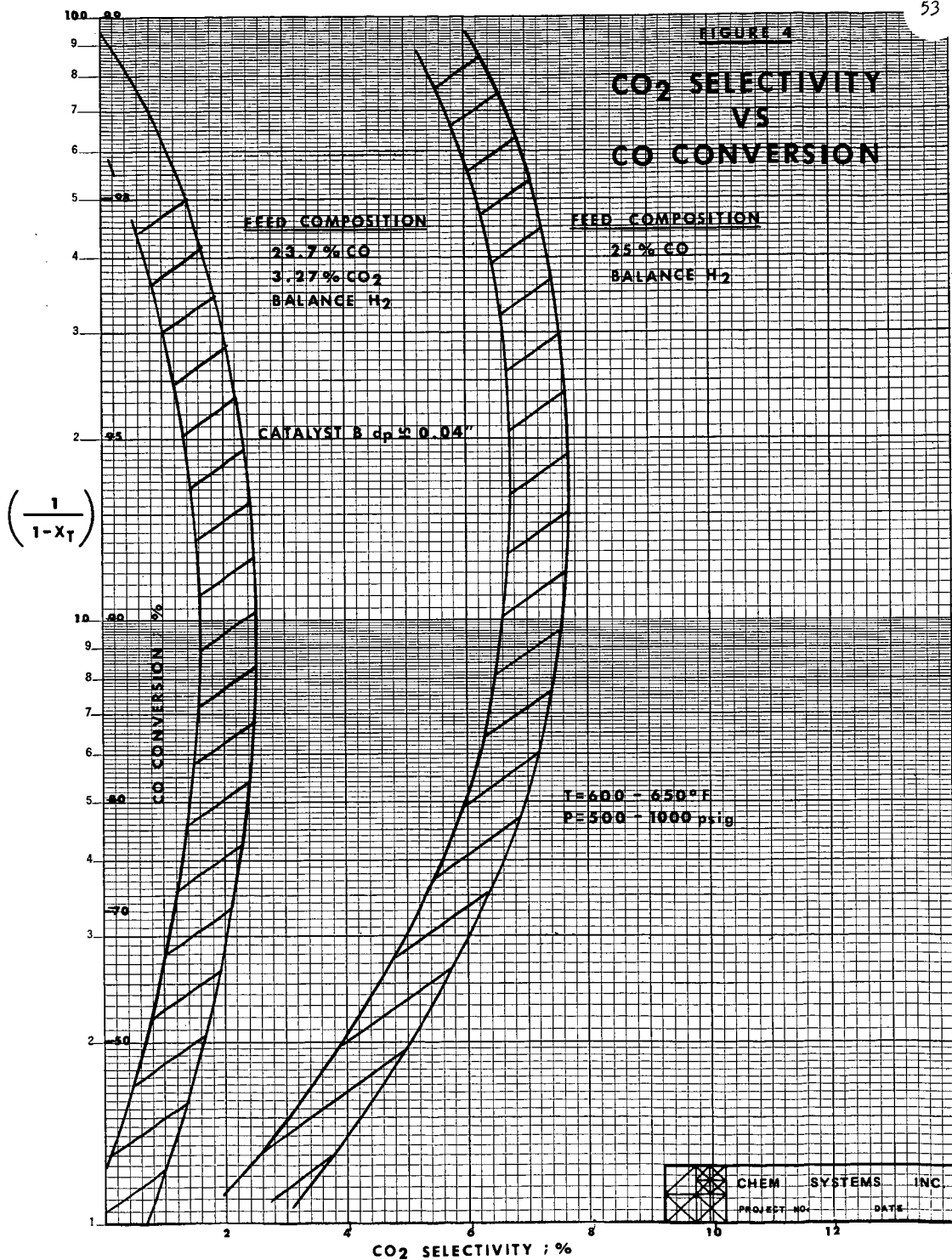
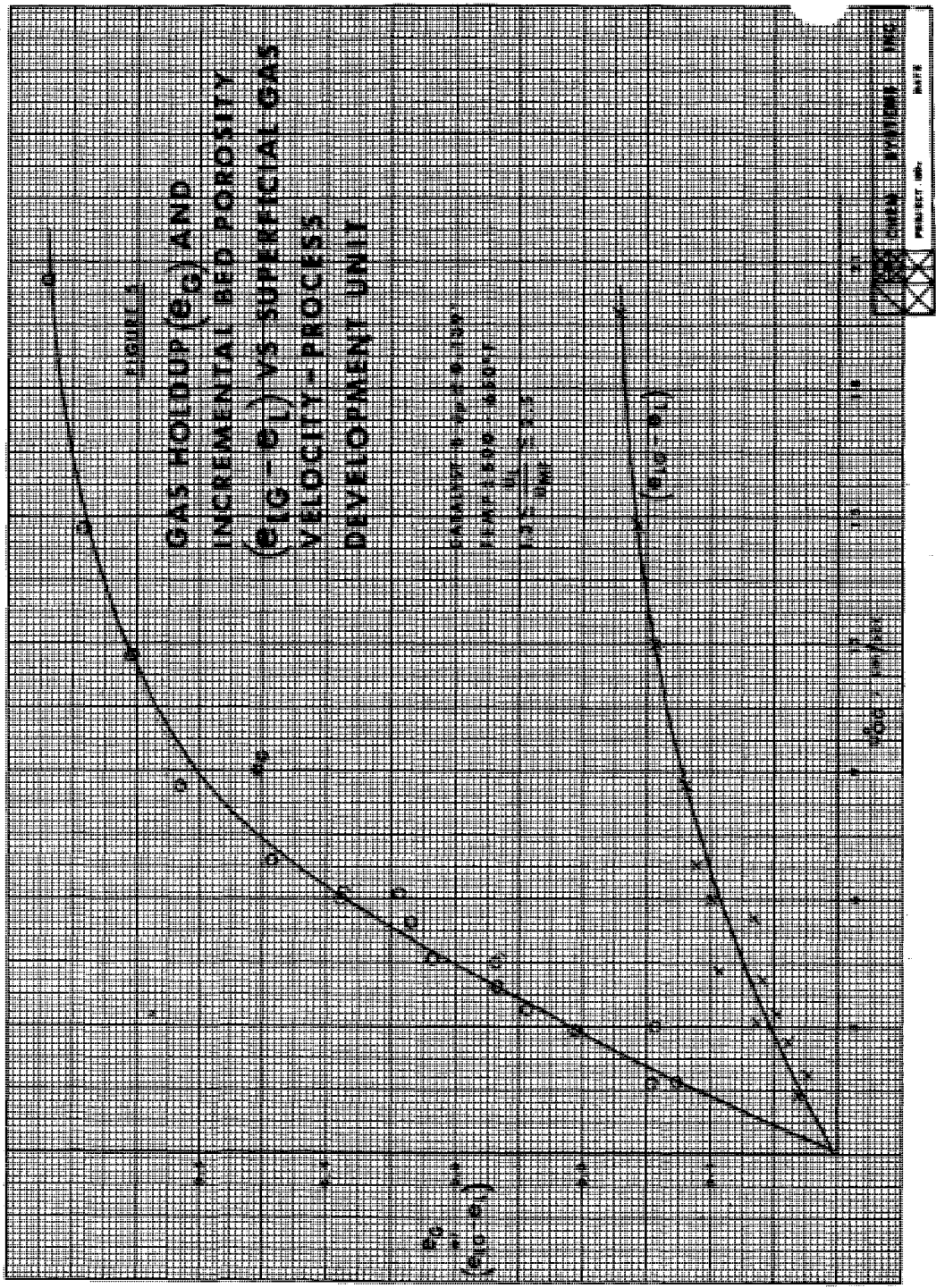


FIGURE 2
GAS HOLDUP (e_G) AND
INCREMENTAL BED POROSITY
($e_G - e_L$) VS SUPERFICIAL GAS
VELOCITY - PROCESS
DEVELOPMENT UNIT

DATA FROM 4-10-65
REACTOR - 100T
TYPE - 100T



PROJECT NO. _____
DATE _____

FIGURE 3

CONVERSION VS CONTACT TIME - PROCESS DEVELOPMENT UNIT

CATALYST: R-08200-1307

TEMP: 6.00 ± 0.01 °F

PRESSURE: 100.0

A: 200

B: 300

C: 400

 $\ln\left(\frac{1}{1-x}\right)$

$$\frac{(P_1 - P_2) \times 10^6}{P_2 (P_1 - P_2)}$$

$$\frac{(100 - 100) \times 10^6}{100 (100 - 100)}$$

$$\frac{0}{0} = 0$$

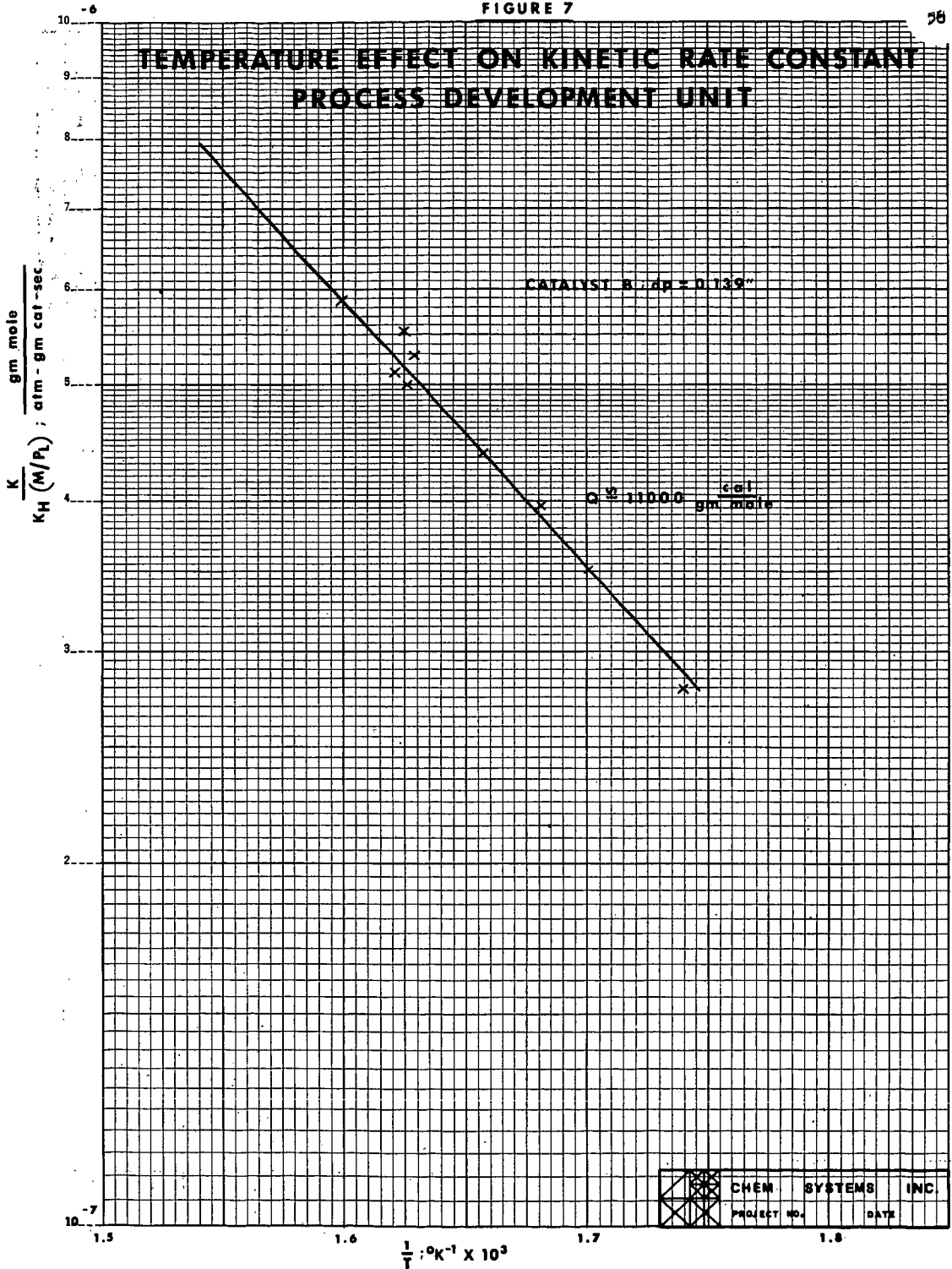
$$\times 10^6$$

DATE	PROJECT NO.	SYSTEM

FIGURE 7

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TEMPERATURE EFFECT ON KINETIC RATE CONSTANT PROCESS DEVELOPMENT UNIT



THE RMPROCESS

G. A. WHITE, T. R. ROSZKOWSKI, D. W. STANBRIDGE

THE RALPH M. PARSONS COMPANY

PASADENA, CALIFORNIA 91124

INTRODUCTION

Current specifications for pipeline gas dictate that most gasification processes require an upgrading of their crude syngas by a stage of methanation. The upgrading reduces the concentration of hydrogen and carbon monoxide while increasing the heating value of each cubic foot of gas. The RMP process has demonstrated an unusual upgrading capability by methanating, without recycle, a crude syngas of approximately 50 percent hydrogen and 50 percent carbon monoxide and containing less than 1 percent methane. The process has exceptionally wide applicability for gases produced by any coal gasification system from near atmospheric pressure to over 1000 psig.

PROCESS DESCRIPTION

In the process, desulfurized syngas flows through a series of fixed-bed adiabatic catalytic reactors. Between reactors, heat is removed from the system by the generation of high pressure steam in conventional heat exchange equipment. As the flow progresses through the series of reactors and exchangers and the bulk of the syngas is methanated, the temperature of the process gas is progressively lowered, finally resulting in an adequately reduced temperature favorable for achieving a high conversion efficiency of hydrogen and carbon oxides to methane.

The series of reactors and exchangers which methanates a raw syngas without pretreatment other than desulfurization, is collectively termed bulk-methanation. The chemical reactions which occur in bulk methanation, including both shift conversion and methanation are moderated by the addition of steam which establishes the thermodynamic limits for these reactions thereby controlling operating temperatures. The flow sequence through bulk methanation is shown in Figure 1.

EXAMPLE AT 400 PSIA

The conditions selected for illustration here include desulfurized syngas available at 700°F and 400 psia, consisting of 49.8 percent hydrogen, 49.8 percent carbon monoxide, 0.1 percent carbon dioxide and 0.3 percent methane. As shown in Figure 1, 40 percent of this syngas is mixed with superheated steam and the mixture enters the first bulk methanator at 900°F. The principal reaction occurring in this reactor is shift conversion with only a minor degree of methanation. The first reactor effluent is cooled and mixed with an additional 30 percent of the syngas to give a mixed temperature of 1000°F into the second bulk-methanation reactor. Again the second reactor effluent is cooled by the generation of steam, mixed with the remaining 30 percent of the syngas to give a mixed temperature of 1000°F as feed to the third reactor.

In the fourth, fifth and sixth reactors, the inlet temperatures are controlled at 1000°F, 600°F and 500°F respectively which results in a bulk methanated product-gas whose composition is shown in Figure 2. The operating temperatures and pressures for each reactor in bulk-methanation are also shown in Figure 2. The residual hydrogen content leaving the sixth reactor is less than 10 volume percent on a dry basis. Such a gas can then be methanated in a final "dry" stage following carbon dioxide removal, to reduce the hydrogen content to below 3 percent, and leaving less than 0.1 percent carbon monoxide.

EXAMPLE AT LOW PRESSURE

A similar set of design numbers are shown in Figure 3 when operating at near atmospheric pressure. Inlet pressure to the first bulk-methanator reactor is 65 psia and the outlet pressure from the sixth reactor is 22 psia. In this case, the total syngas is introduced into the first bulk-methanation reactor together with the total steam. Because the driving force for methanation is proportionately lower at the lower pressure, the outlet temperature even from the first reactor is below 1400°F. Significantly, leaving the sixth reactor, the hydrogen content of the effluent gas on a dry basis is only 12.1 percent at 22 psia compared to 9.3 percent when operating at 312 psia. This relatively small difference is not entirely surprising in view of the lower operating temperature and the large excess of carbon dioxide present in each case which tends to mask the difference in operating pressure.

DESIGN FEATURES

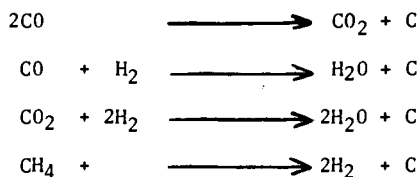
Whether operating at high pressures or low, reactor outlet and inlet temperatures are all conveniently high for the economical generation of 1500 psig steam in conventional heat exchange equipment. Of the total steam produced, approximately one-third is used in the RMP process to accomplish shift conversion, methanation and carbon dioxide regeneration. The mechanical energy of even that portion of the produced steam needed for the operation of the process, will provide a part of the total power requirement of a coal gasification complex by using back pressure turbines. The bulk of the steam produced, approximately two-thirds of the methanation heat, is available as export steam at 1500 psig for any services within a complex.

Now referring back to Figure 1, it is to be noted that there is no separate shift conversion system and no recycle of a product gas for temperature control. Rather, this system is designed to operate adiabatically at elevated temperatures with sufficient steam addition to cause the shift reaction to occur over a nickel catalyst while avoiding carbon formation. The refractory lined reactors contain fixed beds of catalysts and are of conventional designs. The reactors can be a minimum diameter for a given plant capacity since the process gas is once-through only with no recycle, employing less steam than is conventional for shift conversion alone and using a catalyst of a standard ring size of 5/8 x 1/4 inches.

AVOIDING ZONES OF CARBON FORMATION

Before proceeding further with methanation into the cleanup stage, it would be well to review some of the design and operating problems which have been experienced by most developers of methanation systems. Specifically, carbon formation and catalyst sintering are two of the more common problems confronting methanation processes. When considering carbon formation, reference is made to its

potential production from carbon oxides and methane as illustrated by the following equations.



The prediction of conditions favorable for the formation of carbon from these sources can be made by straightforward thermodynamic calculations. However, because a number of other chemical reactions can occur simultaneously and since relative reaction rates are not well known, it is useful to know whether a specified mixture of syngas and steam would have a thermodynamic potential for carbon formation when at chemical equilibrium.

To assist in the proper visualization of multiple chemical reactions occurring simultaneously, we have developed a ternary diagram simplified by considering only the concentration levels of the principal chemical elements present in mixtures of syngas and steam. Carbon, hydrogen and oxygen are used as the identifying elements in our system; these elements are located at the three apexes of the ternary diagram shown in Figure 4. A number of chemical compounds are shown on this figure when the elements are appropriately balanced with one another. Hydrocarbons such as methane and butane are on the left of the figure, carbon oxides on the right and water on the base line connecting hydrogen and oxygen.

Figure 5 has superimposed on the ternary, carbon isotherms for a pressure of 30 psia. Interpretation of the isotherms shows that mixtures of the elements which fall above the curves are in the carbon forming region when at chemical equilibrium. Mixtures of the elements which fall below the curves are outside the carbon forming region at equilibrium. Gas mixtures falling within the family of curves should be at an operating temperature that will carry the specified concentration of carbon in the vapor phase.

Figure 6, which represents a family of carbon isotherms at 400 psia, shows that in certain areas of the diagram, elevated temperatures support higher concentrations of carbon in the vapor phase, but in other areas, lower temperatures favor higher concentrations of carbon. So depending upon the element-mix of gases feeding a methanation reactor, an increase in temperature could cause a mixture to approach a condition where carbon could theoretically be formed. Since these figures are based on equilibrium concentrations of chemical compounds, temperature excursions into the carbon formation region may not result automatically in the formation of solid carbon since such reactions may occur at such a slow rate as to be negligible. On the other hand, it is not good practice to design a system that is normally operating under conditions that are theoretically favorable for carbon formation and depend upon kinetics to keep the operation out of trouble.

The mathematical properties of the set of equations describing chemical equilibrium in the synthesis gas system indicate that the carbon producing regions are defined solely by pressure, temperature and elemental analysis. Once a safe blend of reactants has been determined by use of the ternary, the same set of equations which was used to derive the ternary may be used to determine the gas composition.

Figure 2, gives gas compositions which represent proposed operating conditions at the pilot plant. Figure 7 shows where two compositions are located on the ternary diagram relative to the potential for carbon formation: (1) the feed gas composition to the first bulk-methanation reactor and (2) the product composition from the third reactor which then remains a fixed point throughout the remaining reactors since no addition of gas is made beyond the third reactor. From this figure, it can be seen clearly that sufficient steam has been added to move the mixture well outside the carbon formation region. Even after adding the total syngas to the system, it is not theoretically possible to form carbon when the system is at chemical equilibrium.

It will be quickly recognized that feed-gases to most, if not all, methanation systems for SNG production, are theoretically capable of forming carbon. This potential also exists for feed-gases to all first stage shift converters operating in ammonia plants and in hydrogen production plants. However, it has been commercially demonstrated over a period of many years that carbon formation at inlet temperatures to shift converters is a relatively slow reaction and that once shifted, the gas loses its potential for carbon formation. Carbon formation has not been a common problem at the inlet to shift converters and it has been no problem at all in our bench-scale work and it is not anticipated that it will be a problem in our pilot plant operations.

For a clearer understanding of the behavior of syngases in a shift converter, we have established another set of carbon isotherms when considering the shift reaction only (without methanation) in addition to the carbon forming reactions. Figure 8 shows isotherms at a partial pressure of 270 psia for all components of a gas mixture but excluding methane. Figures such as this are helpful when establishing inlet conditions to reactors since operating data from commercial plants can be used as points of reference.

CLEAN-UP METHANATION

Returning now to the cleanup stage of methanation, Figure 9 shows a system wherein final methanation occurs following gas cooling and removal of steam, and a reduction of carbon dioxide down to approximately 4 percent. Under these conditions, and at a pressure of 300 psia, residual hydrogen is less than 3 percent and carbon dioxide is less than 2 volume percent of the dry product gas following methanation. When operating at near atmospheric pressure, reduction of steam and carbon dioxide are followed by compression to either an interstage level or to delivery pressure for the final stage of methanation. For all pressure levels, the final stage of methanation is outside the region of carbon formation.

Carbon dioxide can be removed from the effluent gas from bulk methanation by any one of several conventional absorption systems. At this point in the process, the gas that must be treated for carbon dioxide removal is less than half of the volume of a shifted gas from which carbon dioxide is normally removed when preparing a syngas to approach stoichiometric concentrations of reactants for methanation. Finally, the gas would be dried to a nominal 7 pounds of water per million scf of gas.

CONCLUSION

Advantages of the RMPProcess are related particularly to cost savings in both capital equipment and operating requirements.

1. Shift conversion. The shift reaction and methanation proceed concurrently without interference over bulk-methanation catalyst thereby eliminating the need for a separate shift conversion operation.
2. Steam utilization. Less steam is employed in the RMPProcess than is required for conventional shift conversion even though in other methanation processes as little as one-half of the total syngas is processed through shift conversion to achieve a near-stoichiometric balance of hydrogen and carbon monoxide for methanation.
3. Temperature control. Temperature control is by steam addition. There is no gas recycle and therefore no recycle compressor.
4. Steam production. The RMPProcess operates at temperatures generally above 1000°F providing a large temperature difference for the production of high pressure steam. Because of this, we can produce more steam and produce it at a higher pressure with less heat transfer surface than other processes.
5. Carbon dioxide removal. Aside from contained carbon dioxide which is removed from syngas when absorbing hydrogen sulfide, the total carbon dioxide produced in the methanation system is removed by conventional absorption in a single stage operation where the volume of gas to be treated is a minimum and the partial pressure of the carbon dioxide is a maximum.
6. Low pressure operation. By using the driving force of a large excess of carbon dioxide for methanation when operating at low pressures, bulk methanation can accomplish a high degree of syngas conversion thereby requiring only a single stage of final methanation following compression to meet pipeline SNG specifications. Such an operation reduces the compression duty by reducing the volume of syngas to a fraction of its original volume while still at low pressure.
7. Space velocity. Most of our experimental data has been developed when operating at a wet outlet space velocity of approximately 10,000 volumes per volume per hour. However, we have data at space velocities up to 25,000. The pilot plant will operate in the range of 5,000 when processing 1 million scfd of raw syngas. Operating on a once-through basis without recycle and at the indicated space velocities, catalyst volumes are a minimum compared with other processes when identical over-design factors are used.

Acknowledgement is sincerely made to Catalyst Consulting Services, Inc. of Louisville, Kentucky, in particular to Dr. Harold W. Fleming, for unusual services of the highest quality while directing the bench-scale experimental program which provides the technical basis and support for the RMPProcess.

FIGURE 1 - BULK METHANATION

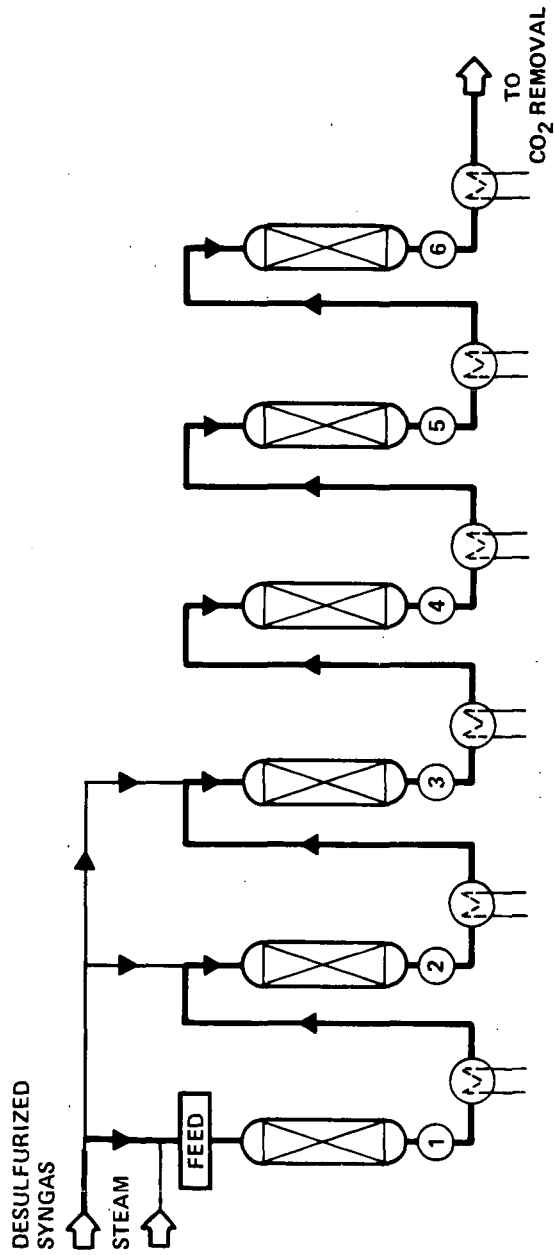


FIGURE 2 - METHANE PRODUCTION @ 400 PSIA

	Feed	-----Outlet-----					
Reactor No.	<u>1</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Composition, Vol %							
H ₂	49.80	54.53	48.07	43.09	36.90	22.86	9.29
CO	49.80	13.97	18.46	20.63	15.25	5.64	.87
CO ₂	0.10	25.80	24.04	23.64	29.21	39.90	46.84
CH ₄	<u>0.30</u>	<u>5.70</u>	<u>9.43</u>	<u>12.64</u>	<u>18.64</u>	<u>31.60</u>	<u>43.00</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Steam/Gas	1.20	0.88	0.56	0.43	0.50	0.65	0.83
Pressure, psia	397	387	372	357	342	327	312
Temperature °F	900	1424	1434	1423	1322	1119	881

FIGURE 3 - METHANE PRODUCTION @ 65 PSIA

	Feed	-----Outlet-----					
Reactor No.	<u>1</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
Composition, Vol %							
H ₂	49.80	54.38	50.36	46.50	36.29	24.00	12.05
CO	49.80	25.37	20.42	16.27	8.24	2.69	0.49
CO ₂	0.10	17.29	21.99	26.06	34.62	41.83	46.45
CH ₄	<u>0.30</u>	<u>2.96</u>	<u>7.23</u>	<u>11.17</u>	<u>20.85</u>	<u>31.48</u>	<u>41.01</u>
	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Steam/Gas	0.48	0.29	0.33	0.36	0.47	0.62	0.78
Pressure, psia	62	57	50	43	36	29	22
Temperature °F	900	1373	1259	1180	1037	884	718

FIGURE 4
Element Coordinates
Raw Materials, Intermediates and Products

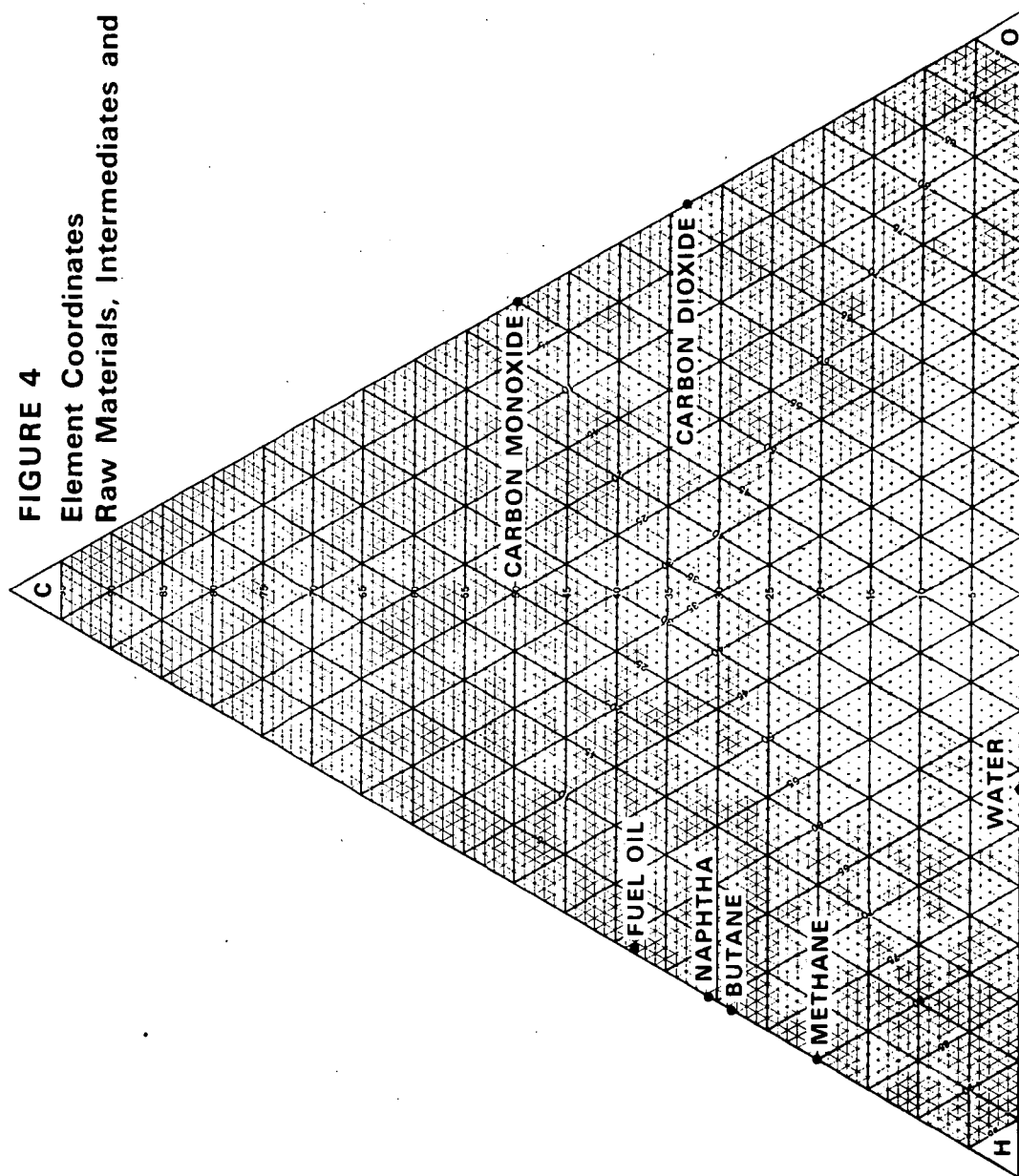


FIGURE 5
Carbon Formation
Equilibrium Isotherms at 30 psia, °F

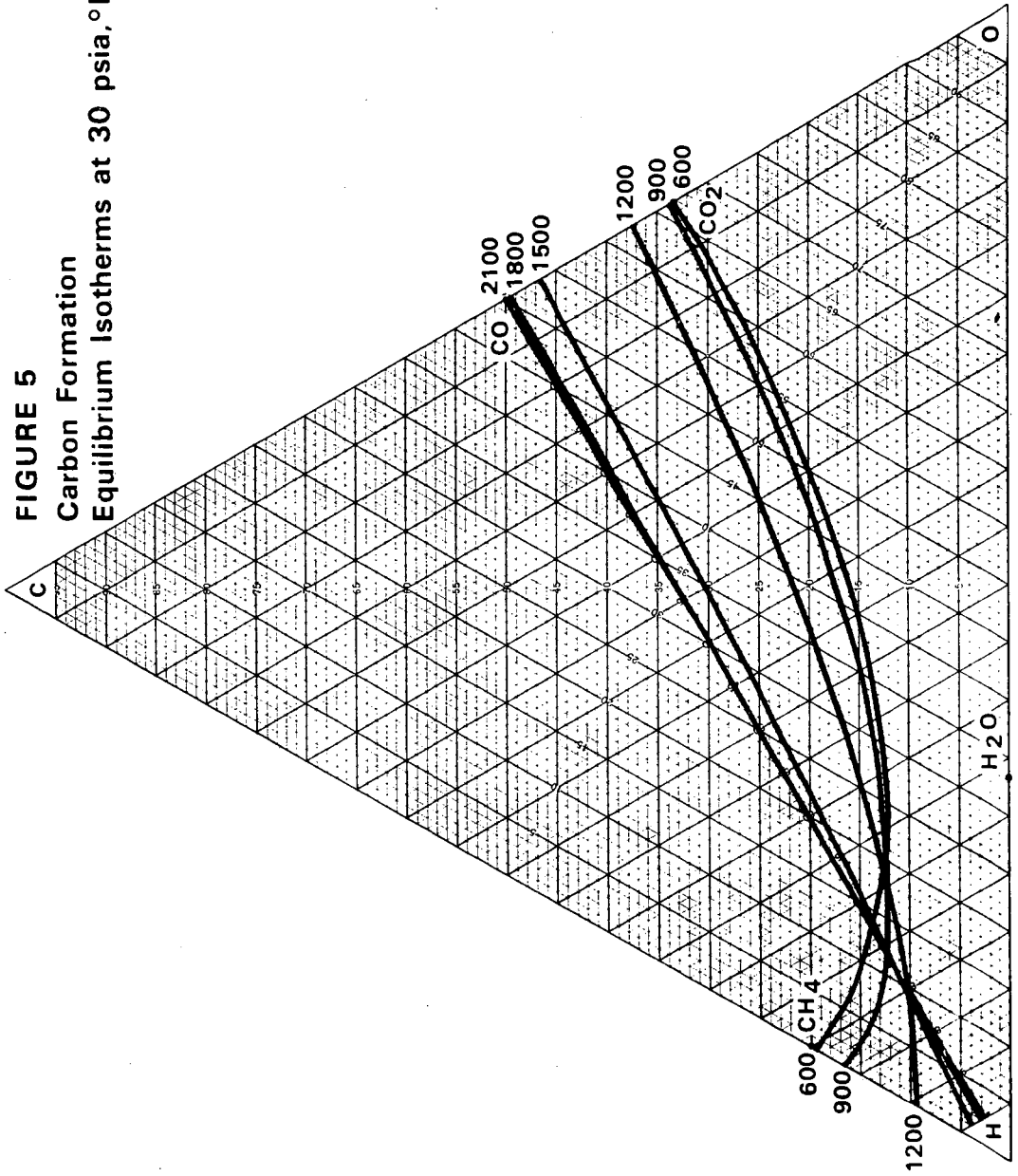


FIGURE 6:
Carbon Formation
Equilibrium Isotherms at
400 psia Total Pressure and °F

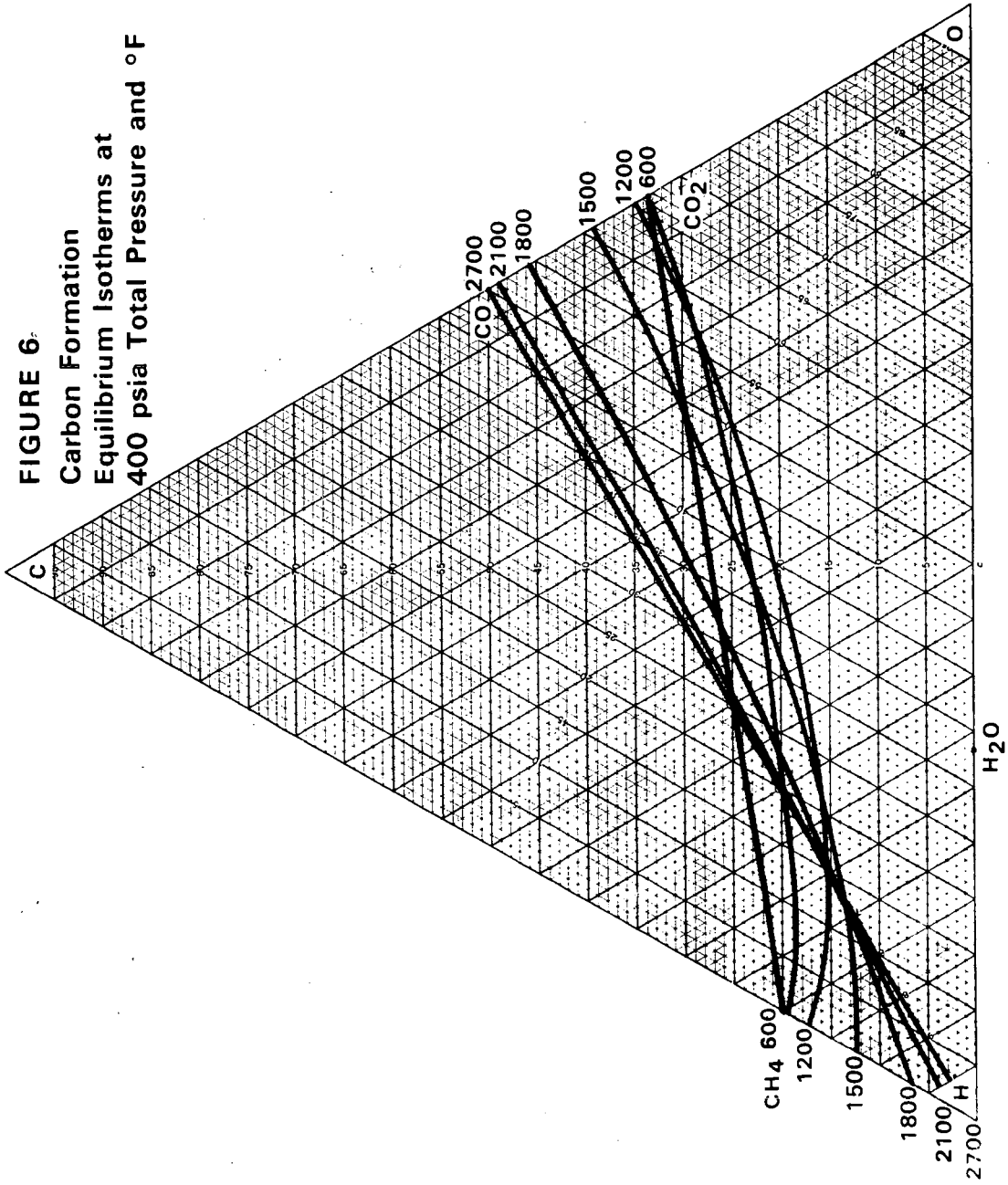


FIGURE 7
Carbon Formation Isotherms at
400 psia Total Pressure and °F
▽ RMPProcess

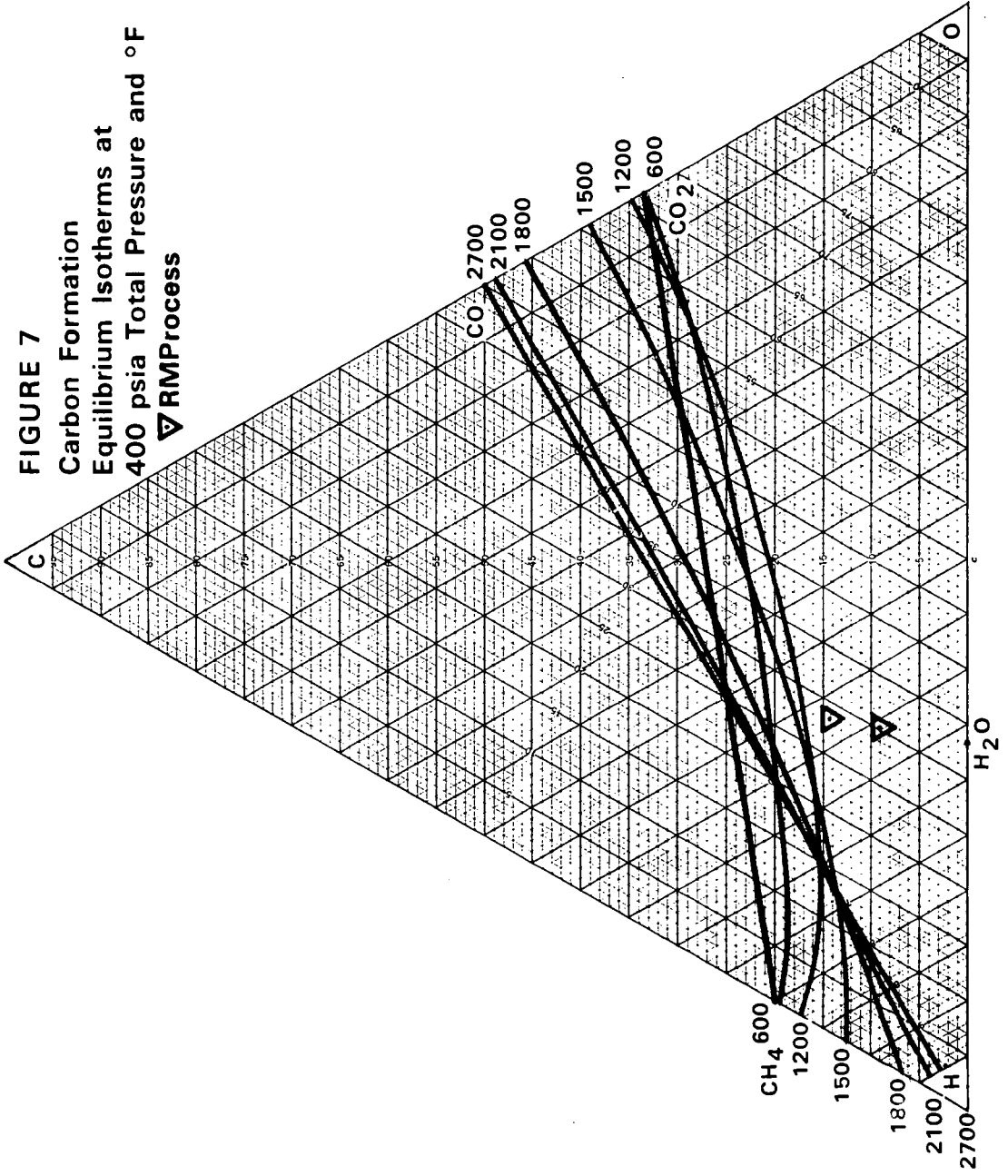


FIGURE 8

**Carbon Formation Isotherms at
Partial Equilibrium Pressure of Hydrogen,
270 psia Partial Pressure of Carbon Monoxide, Carbon Dioxide and
Steam and °F**

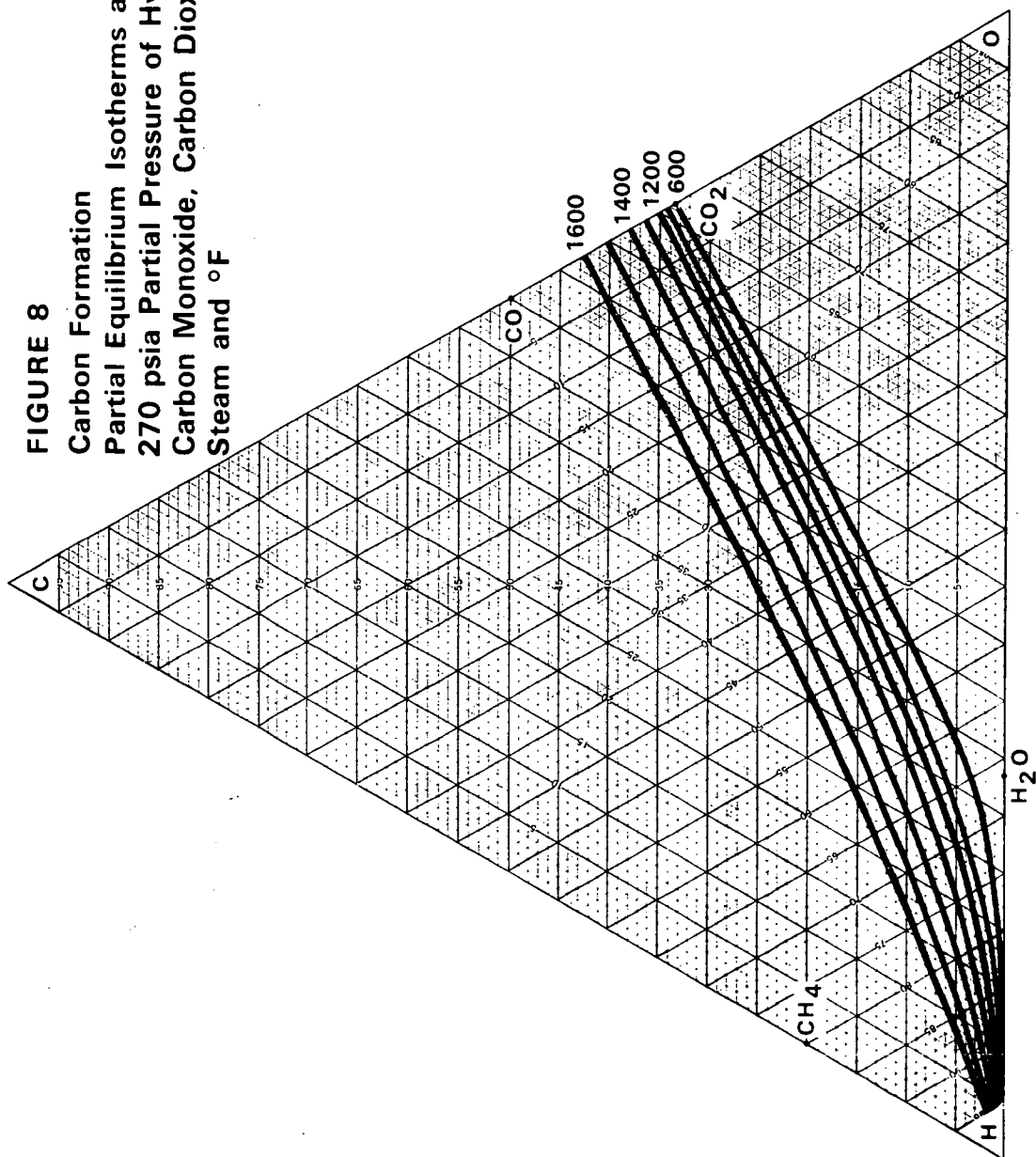
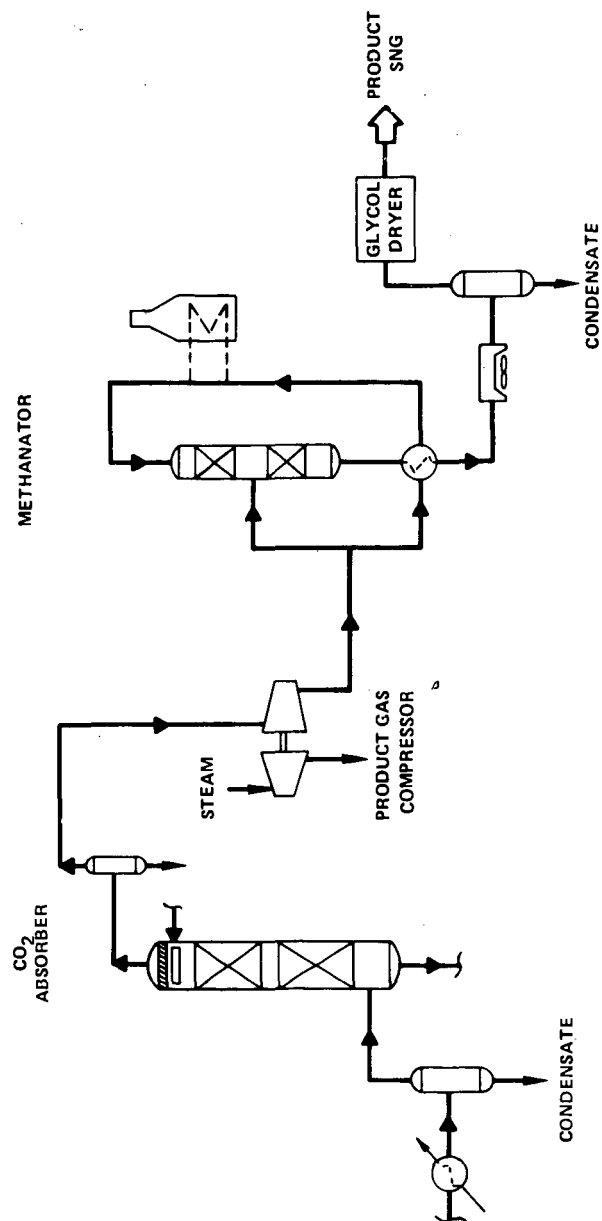


FIGURE 9 - FINAL STAGE OF METHANATION



DEVELOPMENT OF METHANATION CATALYSTS
FOR THE SNG PROCESSES

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ABSTRACT

Laboratory work has continued since late 1970 on developing catalysts for commercial methanation of synthesis gas, produced from coal or naphtha gasification, to a high BTU synthetic gas. Over 160 bench-scale tests, involving over 40 different catalysts have been made to determine the most desirable catalysts. Tests were initially made on commercially available catalysts but results indicated a whole new series of catalysts were required for this application. Tests showed the required catalyst loading, operating conditions, effect of particle size, thermal stability, and resistance to poisoning by trace constituents in the feed gas. The literature on the kinetics of the methanation reactors was reviewed in depth to determine the suitability of previous work on the methanation process conditions which are now planned. The initial kinetic system involving CO and CO₂ methanation along with CO shift was revised after analyzing the data utilizing previously published kinetics. A condensed summary of all the tests made to develop a commercial catalyst and an applicable kinetic system are presented.

DEVELOPMENT OF METHANATION CATALYST FOR SNG PROCESSES

SUMMARY

In the laboratory studies it was shown that methanation activity increases with increasing nickel content of the catalyst while the activity decreases with increasing catalyst particle size. Increasing steam to gas ratio of the feed gas results in increased carbon monoxide shift conversion but does not influence the rate of methanation.

Trace impurities in the process gas such as H_2S and HCl poison the catalyst. The mechanism is different because the sulfur remains on the catalyst while the chloride does not. Hydrocarbons at low concentrations do not affect methanation activity significantly and reform into methane. At higher levels hydrocarbons inhibit methanation and can result in carbon deposition.

A pore diffusion kinetic system was adopted which correlates the laboratory data and defines the rate of reaction.

INTRODUCTION

In late 1970, Catalysts and Chemicals Inc. began a research and development program on methanation catalysts for the production of a high BTU synthetic natural gas from either coal or naphtha gasification. In 1971, Catalysts and Chemicals Inc. entered into an agreement with the El Paso Natural Gas Company to demonstrate the commercial feasibility of the methanation step in the process for the production of synthetic natural gas from coal. The pilot plant was designed in late 1971 and started up in early 1972. Because of the wide spread interest and concern about the methanation step in the over all production of SNG from coal, this project was opened to other participants in 1972. At that time, the Western Gasification Company and COGAS Development Company decided to participate in the pilot plant program.

This paper is a report on the basic work which was done in the laboratory to develop the catalysts for the methanation of synthesis gas from coal and the development of an applicable kinetic system. This report does not include any of the subsequent pilot plant test work which was carried out.

In the laboratory, over 160 bench-scale tests involving over 40 catalysts have been made to determine the optimum catalysts and process conditions for this application. Tests were initially made on commercially available catalysts but early results indicated that a whole new series of catalysts would be required for this application.

The comprehensive research program included all facets necessary for the development of these catalysts. Laboratory tests were conducted to determine the necessary catalyst loading, the design operating conditions, the effect of particle size, the effect of various trace constituents on catalyst performance and finally, resistance of the catalyst to thermal upsets. In this paper only those results which have direct significance to the kinetic model which was selected will be presented.

The laboratory studies which were particularly important to our development of the most active catalyst and the kinetic model for this new methanation application included the following.

TABLE 1

LABORATORY STUDIES

Effects on Catalyst Activity by the:

- Nickel Content of the Catalyst
- Particle Size of the Catalyst
- Steam/Gas Ratio in the Process Gas
- Trace Impurities in the Process Gas

In this paper we have included an extensive discussion of the kinetic system we used and the basis for the selection of this system. During our development work, we frequently referred to the literature and the kinetics reported by previous workers. As a part of this program an extensive literature search was made. The complete bibliography of this literature search is presented for future reference by others.

EFFECT OF NICKEL CONTENT ON CATALYST ACTIVITY

For the methanation reaction, in the process to convert coal to a high BTU gas, various catalyst compositions were evaluated to determine the optimum type catalyst. From this study a series of catalysts were developed to study the effect of nickel content on catalyst activity. This series includes both silica and alumina based catalysts and the nickel content was varied as outlined in Table 2.

TABLE 2
CATALYST DESIGNATIONS FOR
VARIOUS NICKEL CONTENT CATALYSTS

<u>Nickel Content</u>	<u>Silica Support</u>	<u>Alumina Support</u>
50%	C150-1-02	C150-1-03
40%	C150-2-02	C150-2-03
30%	C150-3-02	C150-3-03

This study was run in a laboratory bench-scale unit with 3/4" reactor tubes. The catalysts were sized to 10 x 12 mesh and diluted 9 to 1 with SiO₂ to spread the reaction out through the bed and allow for the measurement of temperature profiles, the profile being an excellent indicator of the catalyst activity. The space velocities were also varied in an attempt to move away from equilibrium CO leakages, so the relative activity of the catalysts could be obtained.

The catalysts were reduced with 100 percent hydrogen at 700°F and an inlet space velocity of 1000 hour⁻¹. Because of the carbon forming potential of a dry gas recycle composition and the cost of reheating the recycle if the water produced by the methanation reaction is removed, this study was made using a wet gas recycle composition. The catalyst loading gas composition and test conditions for these tests are in Table 3 below.

TABLE 3
COAL GASIFICATION PRIMARY METHANATION
TEST CONDITIONS FOR NICKEL CONTENT STUDY

Catalyst Loading

Volume (cc's)	5.0
Size (mesh)	10 x 12
Bed (L/D)	7.31
Bed Dilution	9/1

Gas Composition

% CO	3
% CO ₂	4
% H ₂	12
% CH ₄	81
S/G	.35

Test Conditions

Temperature, °F	500
Pressure (psig)	370
Space Velocity (v/v/hr)	25,000-95,000
Superficial Linear Velocity (ft/sec)	.343-1.302

A brief comparison is given in Table 4.

TABLE 4

NICKEL CONTENT VERSUS H₂ AND CO LEAKAGE

<u>Catalyst</u>	<u>Percent Nickel</u>	<u>Space Velocity (V/V/Hr Outlet Dry Gas)</u>	<u>% CO Leakage</u>	<u>% H₂ Leakage</u>
C150-1-02	50	93,000	0.18	6.93
C150-2-02	40	96,000	0.80	13.10
C150-3-02	30	96,000	3.35	22.30
C150-1-03	50	88,600	0.66	10.70
C150-2-03	40	96,000	0.27	16.88
C150-3-03	30	96,000	1.24	16.40

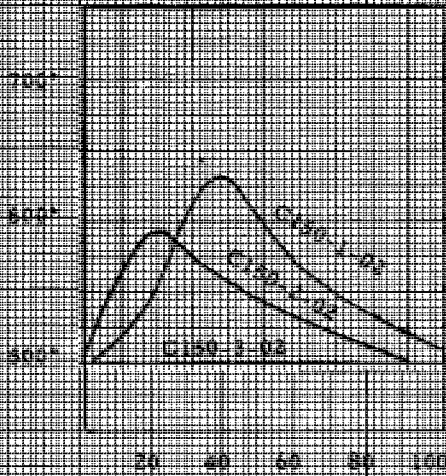
The temperature profiles for each catalyst at two different space velocities are given in Figures 5 and 6.

The lower nickel catalysts demonstrate a reasonable activity but the activity obviously decreases with nickel content. In Figures 5A, 5B, 6A and 6B it can be seen that at approximately 25,000 space velocity the 30% nickel on alumina catalyst uses 50% of the bed to obtain the maximum temperature while at 50% nickel the reaction only uses 30% of the bed. Each of these tests was extended for 300 hours or more. At various times during this study a test condition would be repeated and the percentage of the bed used for reaction indicated the catalyst had not aged.

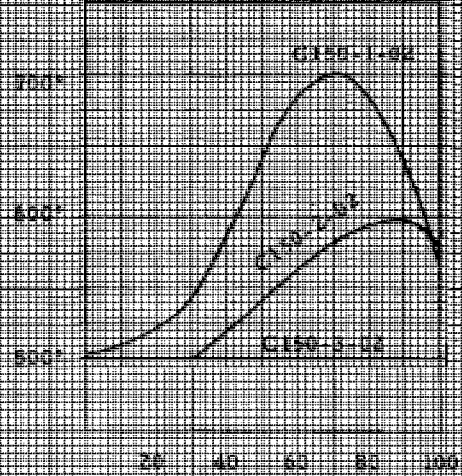
Carbon analysis indicated that no carbon deposition occurred at the conditions of these tests.

TEMPERATURE VS PERCENTAGE OF BED DEPTH

Silica Supported Catalysts

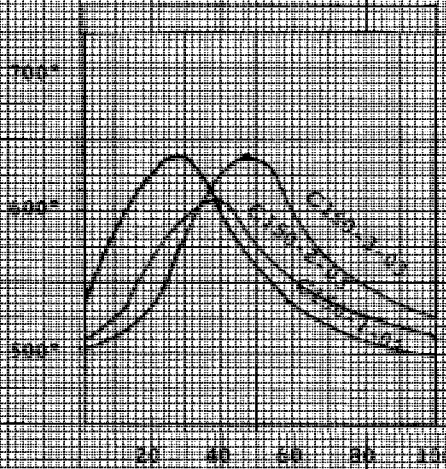


5 A. 25,000 Space Velocity

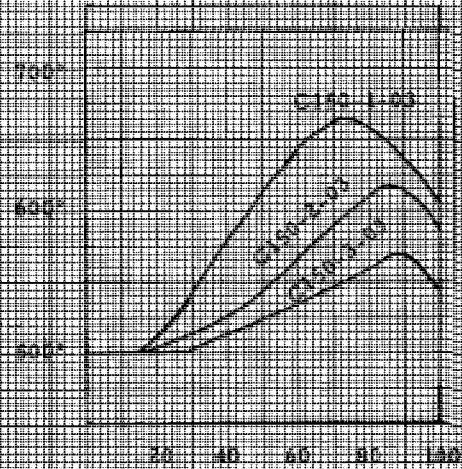


6 A. 25,000 Space Velocity

Alumina Supported Catalysts



5 B. 25,000 Space Velocity



6 B. 25,000 Space Velocity

EFFECT OF PARTICLE SIZE ON CATALYST ACTIVITY

The particle size study was made on the C150-1-02 catalyst. The C150-1-02 oxide mixture was tabletted in three different sizes: $1/8'' \times 1/16''$, $3/16'' \times 3/32''$ and $3/16'' \times 3/16''$.

The catalyst was reduced by the procedure described previously and tested at the conditions of the primary wet gas recycle methanation. The catalyst loading, gas composition and test conditions are outlined in Table 7.

TABLE 7

PARTICLE SIZE STUDY CONDITIONS

Catalyst Loading:

Type	C150-1-02
Volume, cm^3	10.0
Form	Tablets
Size, inch	$3/16 \times 3/16''$, $3/16 \times 3/32''$, and $1/8 \times 3/32''$
Bed Length/Diameter	1.46

Gas Composition:

% CO	5.0
% CO_2	4.0
% H_2	23.0
% CH_4	68.0
S/G	0.35-0.40

Test Conditions:

Inlet Temp., $^{\circ}\text{F}$	500-550
Pressure, psig	350
Space Velocity, $\text{v}/\text{v}/\text{hr.}^{(1)}$	20,000; 40,000; 60,000
Superficial Linear Velocity, $\text{ft}/\text{sec.}^{(2)}$.075-.250

- (1) The space velocity is the volume of outlet dry gas per volume of catalyst per hour.
- (2) The linear velocity is based on 700°F temperature and outlet flow rate.

The results are summarized in Table 8.

TABLE 8

CATALYST PARTICLE SIZE STUDY

Temperature, °F			Space Velocity V/V/Hr.	Outlet Analyses		Activity Constant
Inlet	Hot Spot	Outlet		% CO	% H ₂	Kw CO
C150-1-02, 3/16" x 3/16"						
558	793	742	20,000	<.03	7.3	40,674
556	740	720	40,000	<.03	10.4	36,659
554	728	680	60,000	<.03	14.8	<u>39,407</u>
Avg.						38,713
C150-1-02, 3/16" x 3/32"						
562	778	735	20,000	<.03	7.3	59,788
563	797	730	40,000	<.03	9.9	<u>51,052</u>
Avg.						55,420
C150-1-02, 1/8" x 1/16"						
564	814	730	20,000	<.03	6.8	78,902
565	785	748	40,000	<.03	8.7	66,045
562	807	755	60,000	<.03	12.2	<u>73,464</u>
Avg						72,804

As the particle size decreases, the hydrogen leakage decreases. Also, the hot spot temperature is higher in the bed as the particle size decreases. Both show that the smaller particle size has greater activity. A kinetic system which defines the reaction in terms of CO and CO₂ methanation and CO shift conversion was used to determine the activity as shown in the last column of the table. The relative activity, based on particle size, is given as follows:

Particle Size	CO Methanation	Kw _x /Kw _o
	Kw	
3/16" x 3/16"	38,713	1.00
3/16" x 3/32"	55,420	1.43
1/8" x 1/16"	72,804	1.88

If we assume that the activity is inversely proportional to particle size

$$\frac{Kw_o}{Kw_x} = \left(\frac{D_x}{D_o} \right)^n$$

then n approximately equals 0.9 or Kw is proportional to $\left(\frac{1}{D} \right)^{0.9}$ where D is the

equivalent sphere diameter. Since the kinetics are based on diffusion control it had been assumed that K_w was proportional to $1/D$. This data gives fairly good agreement since the packing and flow in the small diameter laboratory tubes would also cause some error.

EFFECT OF STEAM TO GAS RATIO ON CATALYST ACTIVITY

In the various laboratory studies where the outlet gas composition was not at equilibrium, it was observed that the steam to gas ratio significantly affected the hydrogen leakage while the carbon monoxide still remained low.

Assuming that various reactions will proceed at different rates a study was made to determine the effects of the steam to gas ratio on the rate of reaction. The conditions for this test are presented in Table 9. Results of the test are tabulated in Table 10.

In varying the steam/gas ratio from .15 to .40 significant differences were observed. At the lower steam to gas ratios there is no CO shift conversion. At higher steam to gas ratios there is CO shift conversion.

When evaluating the data as summarized in Table 10 and obtaining activity constants for CO and CO₂ methanation and CO shift conversion, the activity for methanation remains the same regardless of the steam to gas ratio. However, with the high steam to gas ratio, shift conversion is occurring at about 25 percent of the rate of CO methanation. At low steam/gas ratios no shift conversion is observed.

TABLE 9

CONDITIONS FOR STEAM TO GAS RATIO STUDY

Catalyst Loading:

Type	C150-1-03, C150-4-03
Volume, cm ³	10.0
Size, inch	3/16 x 3/32"
Bed, Length/Diameter	1.46

Gas Composition:

% CO	5.0
% CO ₂	4.0
% H ₂	23.0
% CH ₄	68.0
S/G	.15-.40

Test Conditions:

Temperature, °F	500-850
Pressure, psig	350
Space Velocity, v/v/hr.	20,000
Superficial Linear Velocity, ft./sec.	.078

TABLE 10
EFFECT OF STEAM TO GAS RATIOS

EFFECT OF SIBERIAN TO CARBON DIOXIDE																	
Catalyst	Hours On Stream	Temperature, °F				Inlet				Outlet				Equilibrium			
		Inlet		Hot		S/G	Inlet		Spot	Outlet		%CO	%CO ₂	%H ₂	%CO	%CO ₂	%H ₂
		Inlet	S/G	Inlet	Spot		Inlet	Spot		Outlet	Spot						
C150-1-03 50% Nickel on Alumina	33	.365		498	688		4.34	4.13	20.14	.247	5.26	6.45	2.73	.007	3.54	2.73	
	79	.368		499	680		3.42	6.25	14.60	.183	6.34	4.81	2.46	.016	6.50	2.46	
	93	.308		500	637		3.12	1.54	14.30	.165	3.01	4.97	2.35	.001	.933	2.35	
	35	.15		502	765		7.31	4.52	16.90	.459	8.75	2.80	1.52	.022	7.21	1.52	
	40	.15		501	773		7.31	4.52	16.90	.503	8.50	2.24	1.52	.022	7.21	1.52	
	51	.182		502	704		4.28	4.26	14.70	.255	6.10	2.34	2.10	.020	4.86	2.10	
	58	.02		500	824		4.18	5.52	17.70	.167	4.31	1.69	1.83	.080	5.44	1.83	
	61	.02		500	804		4.18	5.52	17.70	.159	4.43	1.69	1.25	.037	5.36	1.25	
65	.02		500	808		4.18	5.52	17.70	.170	4.51	1.82	1.60	.061	5.41	1.60		
C150-4-03 60% Nickel on Alumina	33	.365		498	672		4.34	4.13	20.14	.223	4.53	4.68	2.73	.007	3.54	2.73	
	79	.368		498	666		3.42	6.25	14.60	.114	6.10	3.64	2.46	.016	6.50	2.46	
	93	.308		499	637		3.12	1.54	14.30	.124	2.70	3.36	2.35	.001	.933	2.35	
	35	.15		500	731		7.31	4.52	16.90	.138	8.77	2.69	1.52	.022	7.21	1.52	
	40	.15		499	748		7.31	4.52	16.90	.228	8.50	2.27	1.52	.022	7.21	1.52	
	51	.182		500	680		4.28	4.26	14.70	.139	6.00	1.65	2.10	.020	4.86	2.10	
Catalyst	Hours On Stream	Inlet S/G	Kw CO	Kw' CO ₂	Kw Shift	Average		Corrected to									
						Kw CO	1/4" x 1/4" Tablets										
C150-1-03	40	.15	37,173	29,734	0												
	51	.18	49,564	39,645	0												
	65	.02	45,434	36,342	0	42,336		23,814									
	79	.37	37,173	29,734	13,011												
C150-4-03	40	.15	49,564	39,645	0												
	51	.18	-	-	-	51,216		28,809									
	65	.02	49,564	39,645	-												
	79	.37	54,520	43,610	13,630												

EFFECT OF TRACE CONSTITUENTS IN THE PROCESS GAS ON CATALYST ACTIVITY

In the process to make SNG from coal the methanation feed gas can contain various trace constituents which could affect performance. The coal can contain various amounts of sulfur, chloride and nitrogen. These will mostly be converted to H_2S , HCl , NO_x and NH_3 , the last of which can be scrubbed or condensed out of the gas. These components can then be potential catalyst poisons. In addition to these inorganic compounds, various hydrocarbon compounds will be formed in the gasifier. Most of the heavier components can be separated. However, the C_2 and C_3 hydrocarbons are expected in the methanator feed gas.

Two other components, methanol and benzene, were added to the study. Methanol was included for processes using Rectisol systems for CO_2 removal prior to methanation. Benzene was considered to determine the effect of aromatics on the catalyst activity and potential carbon formation.

In summary, Table 11 shows the components included in this study. The general conditions are tabulated in Table 12.

TABLE 11
COMPONENTS OF TRACE IMPURITIES STUDY

H_2S	RSH and COS were not included since they are expected to hydrogenate to H_2S over the nickel catalyst.
HCl	
NO_x	NH_3 was not included since it can be separated by condensation or scrubbing.
CH_3OH	MeOH is included because of anticipated use of a Rectisol System.
C_2, C_3	Ethane, ethylene, propane and propylene are the expected light hydrocarbons in the process gas.
Benzene	Benzene was included to study the effect of aromatics on the catalyst in the event of catalytic sulfur removal as opposed to Rectisol.

TABLE 12
GENERAL CONDITIONS FOR TRACE IMPURITIES STUDY

Catalyst Loading:

Type	C150-1-03
Volume, cm ³	10.0
Size	10 x 12 mesh

Gas Composition:

%CO	5-7
%CO ₂	4-6
%H ₂	20-25
%CH ₄	62-71

Test Conditions:

Temperature, °F	600
Pressure, psig	350
Space Velocity, V/V/Hr.	10,000
Steam/Gas Ratio	.35

1. Sulfur - Each impurity was added separately to the gas mixture and passed over C150-1-03 to determine its effect on catalyst activity.

These tests were run at the primary methanation conditions, but were run in a small 3/8" tube reactor on sized, 10 x 12 mesh, catalyst. The first test involves the addition of H_2S in the 1-3 ppm range to the dry feed gas. The effect of the H_2S on the catalyst activity is summarized in the following table.

TABLE 13
EFFECT OF SULFUR POISONING

	Initial %-CO Conv.	Initial Kw-CO Meth.	Final %-CO Conv.	Final Kw-CO Meth.	% S Added to Catalyst	Ppm S in Feed	Calculated Inlet Sulfur ppm
Test 1	99.8	81,500	6.4	1,000	0.295	2-3	3.1
Test 2	98.6	65,500	85.5	25,500	0.274	0	0.93
Test 3	98.2	65,000	84.3	25,000	0.125	0	0.26

Tests 2 and 3 were made in the same reactor as Test 1. The catalyst was started up with no sulfur addition to confirm the initial activity. As can be seen from the table in the second and third tests, the catalysts picked up sulfur in both tests and deactivated even though no sulfur was added to the feed indicating that sulfur had remained in the reactor after Test 1. This is a common problem working with sulfur in laboratory test reactors. The sulfur will react with the steel walls of the reactor. Then even though sulfur is removed from the feed sulfur will evolve from the walls of the reactor and either be picked up by the catalyst or appear in the effluent from the reactor. With continuous addition of sulfur the CO leakage continues to increase.

In Test 1 with 3 ppm sulfur in the feed gas the catalyst showed continuous deactivation; it did not maintain some intermediate level of activity. For Tests 2 and 3, the calculated inlet sulfur concentration is shown and this value is calculated based upon the amount of sulfur found on the catalyst and the time on stream. With .13 to .30 percent sulfur on the catalyst, 60-90 percent of the activity was lost. Although Tests 2 and 3 were never conducted as originally planned, feeding 1 ppm sulfur in the feed gas, it was felt that the results of Tests 2 and 3 satisfactorily proved the severe poisoning effect of sulfur on C150-1-03.

RSH or COS as the source of sulfur was not studied because at the conditions of the test they are expected to hydrolyze or hydrogenate to H_2S and poison the catalyst the same as if they were H_2S .

2. Chloride - C150-1-03 was tested at primary wet gas conditions to determine the effect of chloride on catalyst performance. Chloride was expected to be very detrimental to catalyst activity, but the manner of deactivation was uncertain. The chloride was added to the system as hydrogen chloride in the feed water, up to 14 ppm, dry gas basis.

The test was conducted in a single reactor unit with an electric furnace heater. The feed water served as the source of steam and chloride for this test.

Table 13 provides a synopsis of test results as the chloride level was changed. Table 14 shows the change in the hot spot location caused by increased chloride levels.

Analysis of the discharged catalyst is presented in Table 15. New catalyst analyzed less than 0.01 percent chloride.

The chloride level was raised to greater than 5 ppm in the feed gas because the hot spot had moved down to the 69 percent level and remained there. Note that the percent conversion changed significantly only when the hot spot had reached the bottom of the bed. When the chloride was removed, neither the hot spot location nor the percent conversion improved.

Hydrogen chloride is a permanent irreversible poison to the methanation activity of C150-1-03 even though the majority of it is not picked up by the catalyst and is observed in the effluent gas. Only 0.02-0.04 percent was found on the discharged catalyst, but any amount of chloride in the feed gas is detrimental to catalyst activity.

TABLE 13

CHLORIDE POISON TEST

Days		
1 - 5	No Chloride added.	Steady 99.1% conversion of CO with constant hot spot location 31% into the bed.
6 - 21	0.52 ppm Cl added on dry gas basis.	Seemed to be a slight decrease in percent conversion (Avg. = 98.7%). Hot spot moved down into bed to 69% level.
22 - 29	2-4 ppm Cl added on dry gas basis.	The overall average percent conversion was 98.5 during this period. The hot spot remained at the 69% level.
30 - 33	All chlorides were removed from feed.	The conversion did not change when chlorides were removed (98.6%). The hot spot also remained unchanged.
34 - 47	11-14 ppm Cl added on dry gas basis.	The percent conversion steadily decreased during this period of high chloride levels until on the 47th day the conversion was only 84.0%. The hot spot also decreased down into the bed at the 94% level. On the 37th day, the unit had to be shut down to repair a leak on the inlet to the reactor. The catalyst was kept under CO ₂ during this period.
48 - 51	All chlorides were removed from feed again.	The percent conversion continued to decrease. On the 51st day the conversion was 75.8% when the test was stopped. The hot spot remained at the 94% level, nearly at the very bottom of the bed. (See Figure 1)

Chloride Poison Study: ^{TABLE 14} Hot Spot Location Vs. Days on Stream

87

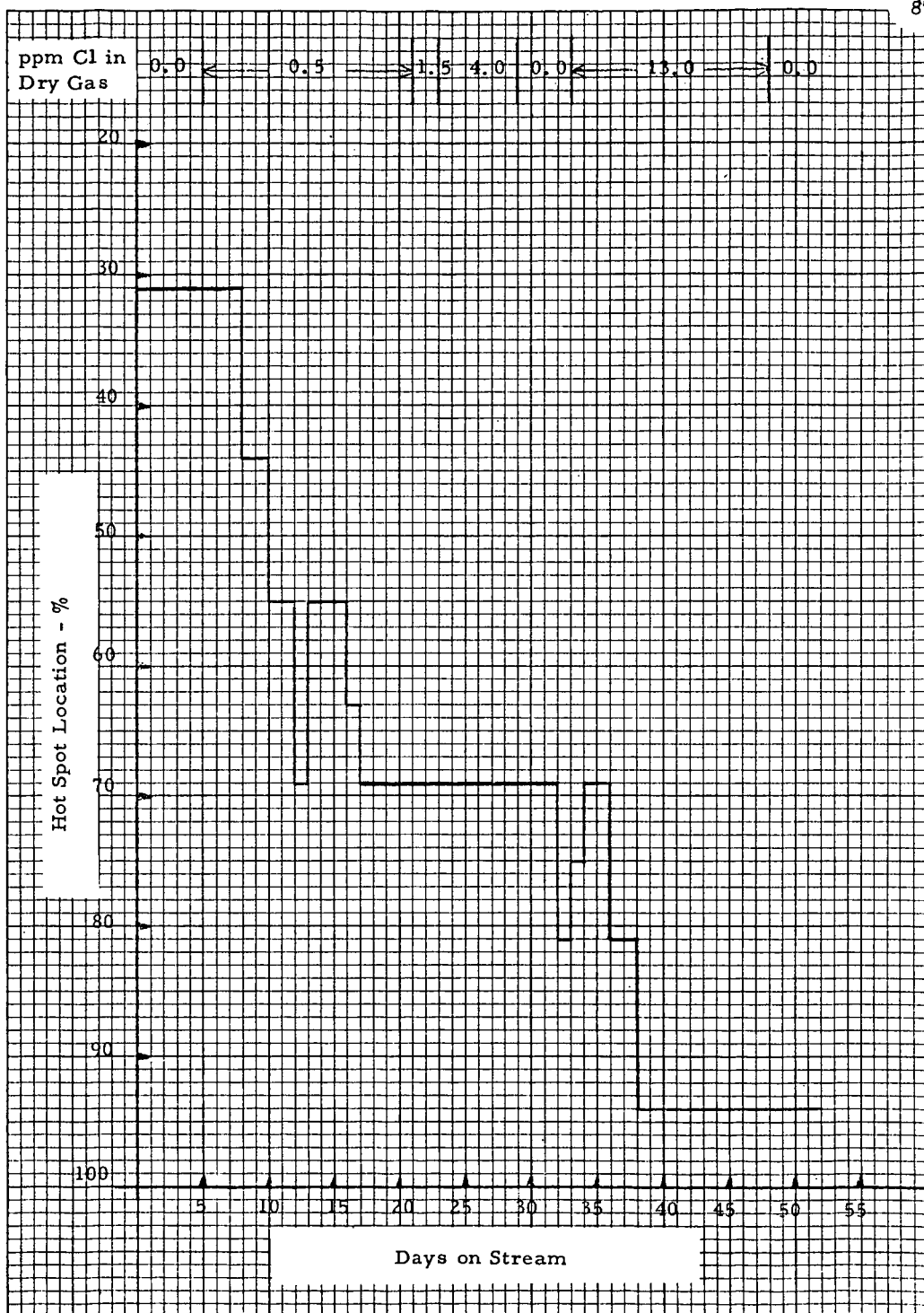


TABLE 15

ANALYSIS OF DISCHARGED CATALYST

	Wt. % Chloride	
	<u>Wet Method</u>	<u>XRF Method</u>
Top 1/3	0.051	0.04
Middle 1/3	0.039	0.02
Bottom 1/3	<u>0.039</u>	<u><0.01</u>
Average	0.043	0.023

3. Nitrogen Dioxide - Nitrogen dioxide can be formed in the gasifier from the nitrogen present in the coal. Since it is an acid gas it was included in the study as a potential poison. This study was conducted with C150-1-03 in the electrical furnace reactor unit. The catalyst was tested at primary wet gas conditions with up to 8 ppm nitrogen dioxide in the dry feed gas. Table 16 provides a synopsis of test results as the NO₂ level was changed.

TABLE 16

RESULTS OF NO₂ ON CATALYST ACTIVITY

<u>Days</u>	<u>Condition</u>	<u>Result</u>
1-8	No NO ₂ Added	Average 99.1% conversion of CO with hot spot location between 31-44% into bed.
9-13	1-2 ppmv NO ₂ Added	Average 99.1% conversion with hot spot location at steady 31%. No change.
14-28	2-7 ppmv NO ₂ Added	Average 99.2% conversion with hot spot location between 31-44% into bed.

Nitrogen dioxide up to 8 ppmv concentration in the inlet gas did not poison C150-1-03 catalyst.

The location of the hot spot fluctuated between 31 and 44 percent levels during this test. The hot spot did not drop sharply down into the catalyst bed as did previous poisoning studies with H₂S and HCl.

4. Alkanes and Alkenes - For this study, C150-1-01 and C150-1-03 were tested at primary wet gas conditions with ethylene, ethane, propylene and propane added to the feed gas. The purpose in testing these hydrocarbons as a possible catalyst poison was to determine whether they would deposit carbon on the catalyst, reform, or pass through without reaction. The test was conducted using the dual-reactor heat sink unit and a water pump and vaporizer as the source of steam. All gas analyses were performed by gas chromatography. The test was stopped with the poisons still in the feed gas in order to preserve any carbon buildup which may have occurred on the catalysts.

The gas analyses, Table 17, show that the catalysts are not visibly affected by these alkanes or alkenes. The CO and H₂ leakages remained low throughout the test, rising slightly after hour 181 when the jacket temperature was raised. The disappearance of the ethane, ethylene, propane and propylene is attributed to reforming reactions taking place, even though a continuous trace ethane leakage was observed. Reforming of such small amounts of hydrocarbons would not create a discernible difference in the gas analyses. There was no downward movement of the hot spot during the test, and carbon deposition did not occur. These observations support our conclusion that ethylene, ethane, propylene and propane undergo reaction over the catalyst but do not poison it.

5. Methanol - In another series of tests, the effect of methanol, which can be carried over from the Rectisol scrubber system, on catalyst activity was determined by adding methanol to the water before vaporizing into the unit. The methanol was added to give .01% to 1.0% on a dry gas basis. Methanol up to 1000 ppm had no effect on activity as evidenced by no change in the H₂ and CO leakages. On increasing the methanol to 1% the temperature profile moved down through the bed but with no noticeable effect on H₂ and CO leakage. On removing the methanol the hot spot returned to its original location in the catalyst bed. The effluent H₂O showed no methanol during the test, indicating that the methanol has reformed to methane.
6. Benzene - Although benzene would ordinarily be scrubbed out by a Rectisol system before the methanators, the possibility of a different H₂S removal system resulted in the inclusion of benzene with our poison study. Benzene could pass through the system, hydrogenate, plug up the catalyst pores or reform.

C150-1-03 and C150-4-03 were loaded into the small dual-tube reactor. The unit was equipped with inlet saturators used as the source of benzene, of which poison levels of 0-5 percent were tested. The results are summarized in Table 18.

The test results show that benzene at low levels had no noticeable effect on activity and was reforming to methane, carbon oxides and hydrogen. At higher levels, greater than 0.5 percent, the activity of the catalyst declined which is demonstrated by the hot spot moving down the catalyst bed and the increase in CO and H₂ leakage. In addition, benzene and cyclohexane were observed in the effluent. At very high levels carbon formation was observed over the C150-1-03 catalyst.

Although benzene is not a poison in the sense that H₂S and HCl are, it is depressing activity by reforming and adsorption on the catalyst, and at high levels can produce carbon.

Poisons not taken into account in kinetics system.

TABLE 17

EFFECT OF LIGHT HYDROCARBONS ON CATALYST ACTIVITY

2150-1-01

INLET C ₃ Stream	Outlet S/G	Temperature of, °F		% of Catalyst Bed Above Hot Spot	GAS COMPOSITION													
					INLET, %				OUTLET, %									
		Top	Hot Spot	Bottom	CO	CO ₂	H ₂	CH ₄	CO	CO ₂	H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₃ H ₆	C ₃ H ₄	C ₃ H ₂	C ₃ H
15	.531	696	696	597	5.07	5.13	26.73	63.07	—	—	—	—	—	—	—	—	—	—
23	.538	751	751	589	5.17	5.43	28.71	60.69	—	—	—	—	—	—	—	—	—	—
73	.536	702	702	591	4.27	4.77	24.38	67.37	—	—	—	—	—	—	—	—	—	—
85	.538	730	730	592	4.92	4.23	24.57	69.67	.186	.473	<.01	3.15	92.09	<.01	.066	<.01	.0021	<.01
111	.537	834	834	620	4.73	6.68	24.90	64.17	.276	.548	<.01	4.04	2.81	94.86	<.01	.072	<.01	.0041
161	.530	826	826	674	4.05	6.77	24.55	69.75	.338	.475	.005	7.21	2.81	90.62	<.01	<.01	<.01	<.01
									.333	.059	.481	.556	<.01	6.32	3.66	85.49	<.01	.0101

2150-1-03

5	.507	728	754	593	5.07	5.13	26.73	63.07	—	—	—	—	—	—	—	—	—	—
23	.484	760	760	600	5.17	5.43	28.71	60.69	—	—	—	—	—	—	—	—	—	—
51	.503	762	762	600	5.06	5.19	25.28	69.01	.447	.088	.491	.162	<.01	5.17	2.21	104.6	<.01	<.01
56	.485	695	721	604	4.91	4.16	21.95	71.80	.443	.093	.608	.669	<.01	5.01	2.36	88.35	<.01	.014
95	.483	683	722	608	4.92	4.23	24.57	69.67	.235	.061	.276	.548	<.01	4.20	2.79	95.48	<.01	.021
111	.505	787	814	644	4.73	6.68	24.90	64.17	.326	.051	.338	.475	.005	7.24	2.05	91.03	<.01	<.01
121	.506	798	798	680	4.91	10.99	26.31	64.35	.353	.045	.321	.547	.0373	11.7	2.71	86.32	<.01	.0018
161	.497	789	806	688	4.05	6.77	24.55	69.75	.333	.059	.481	.556	<.01	6.29	3.20	99.42	<.01	.0039

Discharged Catalyst Properties

	% C	% S	% Reduction
2150-1-01	3.08 (New 2.58)	.048 (New .06)	62.0
2150-1-03	6.14 (New 5.84)	.066 (New .09)	76.3

TABLE 18

EFFECT OF BENZENE ON CATALYST ACTIVITY

Hours Onstream	Catalyst	% Catalyst Bed Above Hot Spot	% Inlet			Gas Composition			% Outlet		
			CO	CO ₂	H ₂	C ₆ H ₆	CO	CO ₂	H ₂	C ₆ H ₆	C ₆ H ₁₂
32 58 123 251 304 335	C150-1-03	0.0	5.91	5.90	23.11	-	.0025	5.45	2.13	-	-
		16.7	5.57	5.76	23.36	.161	.0025	6.99	2.61	-	-
		33.3	3.81	6.34	23.73	.410	.0025	6.32	3.58	.053	-
		33.3	4.31	4.63	26.24	1.86	.01	5.31	7.38	1.281	.04589
		100.0	4.47	7.26	25.79	3.64	.01	6.83	18.93	5.74	.29693
		50.0	3.55	4.98	21.75	-	.01	5.69	12.50	-	-
32 51 84 89 145 251 304 335	C150-4-03	0.0	5.91	5.90	23.11	-	.0025	5.49	1.96	-	-
		16.7	5.98	5.59	24.53	.102	.0025	5.82	2.71	.095	.00037
		33.3	3.81	5.65	23.02	1.09	.0025	5.82	3.05	.297	-
		41.7	3.81	5.65	23.02	.361	.005	6.56	3.22	.720	.00015
		50.0	3.44	5.06	24.5	.404	.005	5.77	4.57	.139	-
		66.7	4.31	4.63	26.24	1.19	.01	5.18	9.06	1.018	.00279
		83.3	4.47	7.26	25.79	5.53	.02	6.02	11.13	7.211	.1443
		66.7	3.55	4.98	21.75	-	.01	5.18	9.35	-	-

DISCUSSION OF KINETIC SYSTEM

In various fields of commercial catalyst practice it has been customary for over thirty years (58) to use a very simple first order, or psuedo first order, equation in preliminary converter design where very great changes of conditions are not made. This equation, for constituent X may be written as

$$\begin{aligned}
 KW &= SVW \log_{10} \left(\frac{\text{Lb. mols/hr. of X in} - \text{Lb. mols/hr. of X}_{eq.}}{\text{Lb. mols/hr. of X out} - \text{Lb. mols/hr. of X}_{eq.}} \right) \\
 &= SVW \log_{10} A
 \end{aligned} \tag{1}$$

In equation 1, KW is a rate constant at a specific pressure and temperature, SVW is total wet gas space velocity, expressed as SCF of total gas per hour per cubic foot of bulk catalyst. X in refers to the lb. mols/hr. of constituent entering the section of catalyst for which the space velocity is measured, whereas X out indicated the lb. mols/hr. leaving the section. X_{eq.} indicates the lb. mols/hr. which would pass through the section under equilibrium conditions. For reactions with large heats, it is necessary to divide a catalyst bed into a number of sections, so that each section is essentially isothermal.

Equation 1 almost necessarily has as its basis the concept that diffusion, either through pores or to the gross surface of the catalyst particle, controls the reaction rate.

Where the control is strictly by the gas film surrounding the catalyst, one would have to convert equation 1 to $KW \sqrt{L} = SVW \log_{10} A$

where L is the catalyst bed depth in feet. This is required because the controlling film thickness is reduced as gas velocities are increased. In general equation (1) is satisfactory for commercial reactors. The differential equation from which (1) may be derived is:

$$- \frac{dX}{dV} = 6.07 \times 10^{-3} KW \left(\frac{\text{Lb. mols/hr. of X}}{\text{Lb. mols/hr. of Gas Flow}} - \frac{\text{Lb. mols/hr. of X}_{eq.}}{\text{Lb. mols/hr. of Gas Flow at equilibrium}} \right) \tag{3}$$

This may also be given as

$$- \frac{dX}{dV} = 6.07 \times 10^{-3} KW (N_x - N_{x eq.}) \tag{4}$$

This refers to the total gas flow, through a plane of catalyst, where N_x is the mol fraction of X in the gas passing through the plane, and $N_{x \text{ eq.}}$ is the mol fraction of X at equilibrium under conditions at this point in the catalyst bed.

Another equation which is helpful for computer use is:

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ &= \left(1 - 10^{\frac{-K_w}{SVW}}\right) \left(\text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}}\right) \end{aligned} \quad (5)$$

In cases where there is no volume change in the reaction, (1) and (5) may be readily derived from (3) or (4).

The solution of equation (3) is complicated when there is a volume change in the reaction which removes constituent X.

For these reactions equation (3) may be used, with dX replaced by ΔX , and dV by ΔV . This may be made as accurate a solution as one wants, if the increments are sufficiently small.

However, equation (5) may be used as is, but a more accurate solution is:

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ &= \left(1 - 10^{\frac{-K_w}{SVW}}\right) \left(\text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}} \times \frac{\text{Flow}}{\text{Flow}_{\text{eq.}}}\right) \end{aligned} \quad (6)$$

Equation (6) has been used in correlating the data of this paper; however, a more accurate approximation solution of (3) is

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{Lb. mols/hr. of X out} \\ &= \left(1 - 10^{\frac{-K_w \text{ Flow}^*}{SVW \text{ Flow}_{\text{eq.}}}}\right) \left(\text{Lb. mols/hr. of X in} - \text{lb. mols/hr. of X}_{\text{eq.}}\right) \end{aligned} \quad (7)$$

Where Flow^* is the volume of gas which would pass if 100% of constituent X were reacted.

Finally, a fairly complicated exact solution of (3) may be derived. It must be noted, however, that equation (3) itself cannot be strictly accurate, since only the diffusion of a single constituent has been considered.

The application of equation (3) to the methanation of CO by the reaction $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$, starting with a mixture of say 90% CO and 10% H_2 , using CO as X, would lead to the erroneous conclusion that methanation is impossible under these conditions. The requirement is that equation (3), operating on one constituent, can only be accurate (even when diffusion is strictly controlling) if X is present at a low concentration. To solve the 90% CO - 10% H_2 case previously mentioned, it would be necessary to consider the diffusion of constituents other than CO.

In view of the above, and the fact that all of the various approximate solutions of equation (3) give about the same answer when the reactant concentration is low, it did not seem worthwhile to work on obtaining better accuracy in the solution of (3).

Equation (7) is, however, of interest when one does comparisons of various kinetic equations. It may be rewritten as

$$\begin{aligned} & \text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X out} \\ &= (1 - 10^{\frac{-K_w}{SVW} x Q}) \left(\text{lb. mols/hr. of X in} - \text{lb. mols/hr. of X eq.} \right) \end{aligned} \quad (8)$$

Thus, (7) is a special case of (8) where

$$Q = \text{Flow}^*/\text{Flow eq.} \quad (9)$$

In computer operations with other kinetic systems equation (8) may be used, and all of the unique features of the kinetic system may be incorporated into the value of Q, which may, of course, be a very complex expression. This technique is only of interest in that it simplifies the work necessary to analyze data using any specific kinetics for a chemical reaction. The technique requires sectioning of the catalyst bed; in most cases with normal space velocities 50 to 100 sections, involving two or three minutes of time on a small computer, appear to be sufficient even when very complex equations are used.

K_w in the foregoing equations is a function of pressure and temperature. Although the effect of pressure and temperature on strictly diffusion controlled processes is small, the effect of these variables on surface reactions is generally quite large. Thus, although diffusion may be the major contributor to the mathematical form of the kinetic equations, a residuum of influence from the basic process taking place at the end of the catalyst pores will also affect the rate constant. The usual balance achieved with respect to pressure is a rate increasing with the square root of the total pressure. Since essentially all of the experimental work in this project was at essentially the same pressure, this study gives no information on the pressure dependance of rate. It should be noted, however, that the form of several proposed kinetic equations (25, 57) would give this type of pressure - rate relationship. Data are available from commercial ammonia plant methanators, and laboratory studies relative to them, which show this type of pressure dependence.

For this reason a square root of pressure term has been introduced into the equation for K_w . Further experimental work would be desirable if pressures greatly different from 25 atm were to be used.

The effect of temperature on K_w has been introduced through an activation energy term. This follows the normal form for this type of reaction, with a very high activation energy below the "threshold" temperature, and a lower value, tending to diminish with increasing temperature, at higher temperatures. This reflects an increasing dependence of reaction rate on diffusion as the temperature is

raised. Activation energies for rate data derived from experiments (7, 28, 30, 32, 48, 50) on the hydrogenation of CO and CO₂ at low pressures and low temperatures using small catalyst particles of .01 to .03 in. diameter generally run from 15,000 to 30,000 cal/g mol. On the other hand, for work at higher pressures and temperatures, with commercial size catalyst (1/8 to 1/4 in. diameter), values of 0 to 10,000 cal/g mol are obtained (32, 33, 25, 50, 57).

In the early phases of study, temperature surveys were run on various catalyst with the object of finding the "threshold" temperature for CO methanation. The following rather typical results were calculated for 1/4 in. C150-1-02 catalyst.

<u>Average Temperature, °F</u>	<u>Kw</u>	<u>Activation Energy, cal/g mol, calc. from previous temperature value</u>
320	170	-
362	710	24,000
389	6020	61,000
416	11850	21,000
529	24300	6,100

In general, considering that these tests are on catalyst which has not been aged, a Kw value below several thousand is indicative of a catalyst not practical for commercial use, so from a utilitarian standpoint these data show a "threshold" temperature slightly below 400°F. Because of the small amount of reaction at the lower temperatures, and the effect of small temperature errors on the activation energy calculation, the three values at low temperatures are not very consistent; however, the average of 35,000 cal/g mol is not in bad agreement with the results of other investigators. The value of 6100 cal/g mol is typical for the diffusion control region.

An examination of laboratory data on C150-1-01 and C150-1-02 catalysts for CO hydrogenation tends to show essentially no change in Kw value between 500, 600 and 700°F. This would suggest an activation energy of zero. Although these data show a small, essentially zero, temperature dependence from 500-700°F (33) the difficulties in unraveling the relationship between the rates of CO and CO₂ methanation, and the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$) prevent one from getting a good value for the activation energy for any one reaction. Considering these tests, as well as various literature studies (32, 33, 25, 50, 57) an activation energy of 5,000 cal/g mol was used below 700°F, and 2,000 cal/g mol above 700°F. One must bear in mind that below the "threshold temperature" any predicted performance would be virtually meaningless. It may be noted that a kinetic equation which in practice is very close to the simple Kw expression (25, 57) uses a 6900 cal/g mol over the entire temperature range (525 - 900°F).

Finally, one needs to know the effect of catalyst particle size on Kw. For a pore diffusion controlled reaction activity should be inversely proportional to catalyst particle diameter; that is, directly proportional to external catalyst surface area.

Several studies (48, 50, 51) show that above 400°F, pore diffusion will control catalyst activity if the particle diameter is above .02 to .03 in. This is far below any practical commercial catalyst particle diameter.

In this investigation (Table 8) values of Kw for CO hydrogenation were found to be dependent on the 0.9 power of the reciprocal of the particle diameter. In view of this, and the literature results, a linear (first power) dependence on reciprocal of particle diameter was used in the Kw expression. Measurement accuracy is certainly insufficient to distinguish between a 0.9 and 1.0 power dependence.

If KWS is a standard value of Kw at a base temperature in °Rankine (TB), a base absolute pressure, PB, and a base catalyst particle diameter, DB, then, at other values of temperature (°R=T), and pressure, P, and catalyst diameter D,

$$KW = KWS \sqrt{\frac{P}{PB}} \times \frac{DB}{D} \times FW \times 10^{-.3934 \Delta H \left(\frac{1}{T} - \frac{1}{TB} \right)} \quad (10)$$

FW in commercial reactors is near one; it is the ratio of number of catalyst tablets per cubic foot to the number per cubic foot one would have in a reactor of infinite diameter. P and PB, and D and DB must be in consistent units.

Where two activation energies are used, TB should be the temperature at which the change is introduced. Thus, in our system TB is 1159.67 (700°F), and 2000 is used for Delta H if T > 1159.67, and 5000 if T < 1159.67.

The value used for PB is one atmosphere, and since activity calculations are made by computing the square feet of catalyst area per cubic foot of catalyst, this amounts to using a standard DB of 45.144 inches in a reactor of infinite diameter.

Where DV is vessel diameter (in the same units as D),

$$FW = 1 - .4912 D/DV \quad (11)$$

A characteristic of most equations for surface controlled kinetics, as opposed to diffusion controlled kinetics, is a number of partial pressure terms, often to high powers. When large changes in partial pressures are made, differences between observed and calculated reaction can easily equal a factor of 1000 or more. Where diffusion type kinetics are used, one seldom finds differences of more than a factor or two or three. While this may not seem very accurate, the comparison between the two methods can be rather startling.

Table 19 compares activities of two catalysts, C150-1-01 and another commercial catalyst. First, from literature data, a catalyst activity is obtained using their kinetics, and another by using equation (5). Then, from typical data taken on the C150-1-01 catalyst, the same procedure is followed. Table 19 reports the activity ratios that are obtained.

It is evident that the equation for reference 1 has broken down completely for CO hydrogenation. The other equations for CO hydrogenation give correlations similar to those obtained by the simple kinetics. These equations are all, however, of relatively simple form. They use low activation energies, and in general, would show an activity dependence on the square root of the pressure, similar to that of the simple kinetics.

For the CO₂ kinetics, the literature kinetics gives more reasonable correlation than the simple, though the difference is not great. However, reference 4 involves methanation of over 50% CO₂ in H₂, under conditions where equation (3) would break down, and 12 involves only the initial hydrogenation (less than the first one or two percent) of the CO₂ present. Furthermore, there is a possibility that the reverse shift would produce enough CO to poison the CO₂ methanation in these experiments, which would make it difficult to obtain agreement between various runs.

TABLE 19

RATIO OF C150-1-01/OTHER COMMERCIAL CATALYST

Reference	Reactant	Literature Equation	Activity Ratio, Literature Equation	Activity Ratio, Equation 3, Approximation Equation 5
1	CO	$r = \frac{pCOpH_2^3}{(A+BpCO+DpCO_2^4 + EpCH_4)}$	9000	5.8
33	CO	$r = \frac{1.1pCOpH_2}{1 + 1.5pH_2}$	$1/2$ 1.2	2.3
2	CO	$r = \frac{KpCOpH_2}{1+K_2pH_2+K_3pCH_4}$	$1/2$ 2.3	2.6
4	CO ₂	$r = \frac{C_1pCO_2pH_2^2}{(pH_2^{1/2}+C_pCO_2+C_3)}$	2.2	3.9
12	CO ₂	$r = \frac{kpCO_2pH_2^4}{(1+K_1pH_2+K_2pCO_2)^5}$	6.2	13.1

A number of measurements made on the methanation of CO_2 may be correlated using equations (5) and (10), with the same values of ΔH as for the CO hydrogenation. Based on diffusion considerations, the value of KWS for CO_2 hydrogenation was taken as 0.8 of that for CO.

Attempts were made to correlate data where both CO and CO_2 were methanated, using simple diffusion for both, with the CO_2 rate set at 80% of the CO rate. In order to get good agreement with experimental data it is necessary to introduce a variable water-gas shift reaction activity.

An examination of some laboratory runs with diluted C150-1-02 catalyst can illustrate this problem. In one run, with 579°F inlet, 598°F exit, 97297 outlet dry gas space velocity, the following results were obtained after minor corrections for analytical errors. 99.9885 percent of the CO present (out of an inlet 2.04 mol %) disappeared in reaction, while the CO_2 present (from an initial 1.96%), increased by over 30%. Equilibrium carbon oxides for both methanation reactions was essentially zero, while the equilibrium CO based on the water-gas shift reaction at the exit composition, was about one-third of the actual CO exit of 0.03 mol %. From these data activities for the various reactions may be estimated, based on various assumptions. Table 20 shows the effect of two differing assumptions.

TABLE 20

Water-Gas Shift Kw	350000	50000
CO_2 Methanation Kw	56000	0
CO Methanation Kw	70000	150000

For the first assumption, the value of Kw for shift appears too high. It must be this high because of the necessity of making CO_2 appear while both CO_2 and CO are being consumed rapidly by methanation. The data may be tested to see if the indicated rate appears unreasonable from the standpoint of mass transfer to the gross catalyst surface.

Regardless of the rate of diffusion in catalyst pores, or the surface reaction rate, it is unlikely that reaction can proceed more rapidly than material can get to the gross pill surface unless the reaction is a homogeneous one, catalyzed by free radicals strewn from the catalyst into the gas stream.

The following equation has been derived for testing mass transfer limitation to the gross catalyst particle (56).

$$Kw = \frac{8100}{D} \sqrt{\frac{L \times SVW}{M \times D \times T}} \quad (12)$$

Here M is average molecular weight of the gas, T is temperature in °Rankine, D is catalyst particle diameter, inches, and L is bed depth in feet. For this calculation, involving a diluted bed, SVW and L must be computed as if all of the active catalyst were gathered into one place. In this experiment L is then .02 feet, SVW is 130000 (counting the steam present), D is .078 in., M is about 16, and T is 1048. This leads to a limiting Kw of about 150000.

Although 150000 is somewhat of an average value of expected maximum Kw, and uncertainties in the computations make the minimum Kw about 15000, below which no mass transfer to gross surface could be expected to be limiting, whereas the maximum possible Kw might be over 1000000, assumption 2 certainly gives the more reasonable explanation of the data.

Many references discuss the inhibition of CO₂ methanation by CO (15, 30, 37, 42, 48, 49, 51). At 320°F, and 300 psig, there is indication that as little as 65 ppm of CO would stop CO₂ methanation (51). Under atmospheric pressure, with .015 inch catalyst (48) CO poisoning of CO₂ methanation was shown with 200 ppm of CO, at up to 446°F.

It is to be expected that the poisoning of the CO₂ methanation by CO will be observed at lower CO concentrations when catalyst particle diameters are smaller. This is because the smaller particle will be poisoned throughout, whereas at some depth in the pores of larger sized catalyst the poisoning effect will drop off, and some significant methanation of CO₂ be permitted to take place. It is noteworthy that the only results in this investigation, such as those considered in Table II, where poisoning was likely at very low CO concentrations, were obtained with very small catalyst particles.

It is concluded that a fully satisfactory system for calculating simultaneous reactions of CO and CO₂ with H₂ and H₂O will require a schedule of the effect of CO on CO₂ methanation as a function of temperature. This effect will probably be different with different particle sizes. From a commercial standpoint the possible size range may be too small to require much difference in the treatment, but in laboratory somewhat lower than the CO methanation rate. A simple kinetics system, such as that derived from equation (3), may be satisfactory for all the reactions. It is unlikely that reliable data will soon be collected for the shift reaction (since it is of a somewhat secondary nature and difficult to study by itself) to justify a more complicated treatment.

For CO methanation one of the simple literature kinetic systems (25, 57) should be as reliable or better than the one used in this study. With CO_2 methanation it is less certain that a simple system is indicated. It is probably of more urgency to elucidate the quantitative effect of the CO on the CO_2 methanation than to find a complex kinetic expression for the $\text{CO}_2\text{-H}_2$ reaction itself.

It is expected that the actual rate of CO methanation will always be high, at least under industrial conditions, whereas the CO_2 methanation rate will vary from about the same as the CO rate down to zero, depending on the operating pressure, temperature, CO content of the gas, and catalyst particle size. Meanwhile a water-gas shift (or reverse shift) reaction will be going on at all times at a fairly high rate.

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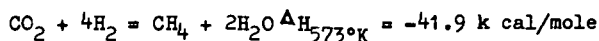
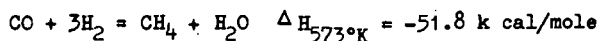
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George W Bridger and Colin Woodward

Research Department, Imperial Chemical Industries Limited, Agricultural Division,
P O Box 6, Billingham, Teesside, TS23 1LE, England

Introduction

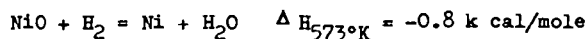
Methanation is the final stage in the purification of synthesis gas in which small concentrations of CO and CO₂ (0.1 - 0.5%) are removed catalytically by reaction with hydrogen:-



The methanation process commonly operates at pressure up to 30 atm and, with the nickel catalyst which is almost universally used for the process, the inlet temperature is about 300°C (570°F). Almost complete conversion of the oxides of carbon occurs giving a product synthesis gas containing less than 5 ppm CO + CO₂. The temperature rise for the exothermic methanation reactions is typically 35°C (60°F).

Catalyst Formulation

The catalysts used in the process are essentially nickel metal dispersed on a support material consisting of various oxide mixtures such as alumina, silica, lime, magnesia and compounds such as calcium aluminate cements. When the catalyst is made the nickel is present as nickel oxide which is reduced in the plant converter with hydrogen, usually the 3:1 H₂:N₂ synthesis gas:-



The heat of reaction is negligible and there is no significant change in temperature in the catalyst bed during reduction. Design limitations in most modern plants require that the catalyst should preferably be reduced at its normal operating temperature, around 300°C (570°F). Once some metallic nickel has been formed, however, methanation begins with the corresponding temperature rise which accelerates reduction of the catalyst further down the reactor. Clearly, the reduction process will continue after the reactor is on-line so that it is common for the activity of the catalyst to continue to increase for some time until an equilibrium state, corresponding to a particular degree of reduction of the nickel, is reached. If engineering considerations permit, the reduction process can be accelerated without detrimental effect upon the catalyst by increasing the temperature to ~660°F.

A good methanation catalyst is one which is physically strong, reducible at 300°C (570°F) and has a high activity. In order to provide a long life, it must retain these properties in use. Commonly lives of 3-5 years are obtained from charges of ICI catalyst 11-3, depending on the temperature of operation and the presence of poisons in the synthesis gas, factors which are discussed later relative to catalyst life. These properties can be obtained by careful attention to the formulation and manufacture of the catalyst.

Methanation activity is related to the surface area of the nickel metal obtained when the catalyst is reduced. The highest surface area of metal and the highest activity are obtained when the nickel is produced as very small crystallites, usually below 100 Å in diameter. One of the functions of the other oxides in the catalyst is to support this fine dispersion of nickel crystallites so that they are available for reaction. The oxides mixed with nickel also retard growth or

sintering of the metal to form large crystallites with a lower surface area and lower activity. The nickel can be dispersed among the other oxides in various ways producing different degrees of mixing e.g. by impregnation of a preformed oxide support with a soluble nickel compound, or by coprecipitating a nickel compound together with the other materials such as aluminium or magnesium as hydroxides or carbonates. These materials are worked up by drying, decomposing etc. and pelleting or extruding precipitated materials, to produce the final catalyst.

Intimate mixing of the components can lead to the formation of compounds or of solid solutions of the components which are difficult to reduce at 300°F but which, when reduced, contain well dispersed and well stabilised nickel. Methanation catalysts in practice therefore are compromises which achieve an optimum reducibility with activity and stability.

An example of compound formation is provided by alumina which, with nickel oxide, readily forms spinel compounds of the type $\text{NiO} \cdot \text{Al}_2\text{O}_3$. A temperature around 1000°C (1800°F) is necessary for combination when NiO is mixed with α - Al_2O_3 but with finely divided NiO and γ - Al_2O_3 temperatures around 500°C (930°F) are sufficient. When the oxides are coprecipitated "spinel precursors" can be detected in the dried precipitate and such catalysts have to be reduced at temperatures as high as 500°C (930°F). They are, therefore, unsuitable for use in conventional ammonia synthesis methanation units.

Magnesia forms solid solutions with NiO. Both MgO and NiO have face-centred cubic lattices with NaCl - type structures. The similarity between the ionic radii of the metals ($\text{Ni}^{2+} = 0.69 \text{ \AA}$, $\text{Mg}^{2+} = 0.65 \text{ \AA}$) allows interchangeability in a crystal lattice and thus the formation of solid solutions of any proportions of the two oxides is possible. Such solid solutions are more difficult to reduce than separate NiO. Thus Takemura et al (Ref 1) showed that NiO reduced completely in the range 230° - 400°C (440° - 750°F) while a 10% NiO - 90% MgO solid solution reduced in two stages, one in the range 230° - 400°C and the other in the range 500° - 600°C (930° - 1100°F). For ease and completeness of reduction in a methanation catalyst, therefore, excessive solid solution formation should be avoided. As indicated above however solid solution formation is beneficial in retarding crystal growth of NiO during manufacture and of reduced Ni during operation. During manufacture a precipitated nickel compound such as the carbonate has to be converted into nickel oxide and, in order to obtain small NiO crystallites, it is desirable that the calcination temperature should be the minimum compatible with efficient conversion of NiCO_3 to NiO. Differential thermal analysis (Figure 1) shows that this endothermic process occurs in two main stages with maxima around 150°C (300°F) and 340°C (640°F) and that the presence of a proportion of magnesia in a solid solution raises the required temperature by only about 15°C (25°F).

This presence of MgO, however, does retard the growth of NiO during calcination as shown in figures 2, 3 and 4. Figure 2 shows, for example, that calcination at 500°C (920°F) for 4 hours results in an increase in NiO crystallite size to 300 - 400 Å whereas, after the same treatment, the crystallite size of an NiO-MgO solid solution (60 - 40 w/w) would be only about 80 Å. Figures 3 and 4 show the effect of duration of calcination on crystal growth at different temperatures. Crystallite size is proportional to $T^{0.25}$ for NiO alone, and proportional to $T^{0.12}$ for NiO-MgO and for MgO alone.

Figure 5 shows the effect of calcination temperature on the subsequent activity of the catalyst after reduction at 300°C (570°F). These activity measurements are made in laboratory tubular reactors operating at 1 atmosphere pressure, inlet gas composition CO 0.40%, N_2 25%, H_2 74.6% and inlet temperature 300°C. Conversion of CO is measured and the catalyst activity expressed as the activity coefficient, k , in the first order equation :

$$\text{rate} = k p_{\text{CO}} P^{0.3} \left(1 - \frac{K}{K_p}\right) e^{-\frac{e}{RT}}$$

The reducibility of the catalyst is demonstrated in Figure 6 which shows the activity of catalysts, measured as described above, after reduction to constant activity at temperatures in the range 280° - 350°C (530° - 660°F). It will be seen that catalyst 11-3 compares favourably with other catalysts which contain larger amounts of alumina and consequently are more difficult to reduce at acceptable temperatures.

In summary, therefore, we have found it beneficial to include a small amount of MgO (2 - 3%) in ICI methanation catalyst 11-3. This provides the ideal compromise between ease of reducibility and sintering resistance. By this means, a catalyst is produced which is readily reduced at 300°C - 350°C (570° - 660°F) but with which loss of activity caused by sintering is not a problem during several years' normal operation at temperatures up to 350°C (660°F). This good performance has been confirmed by experience in many plants including ICI's three 1000 ton/day ammonia plants at Billingham, England.

Poisons

With a well constituted catalyst of this type, at normal operating temperatures sintering is not an important cause of loss of activity even if the catalyst is occasionally overheated. The principal cause is poisoning. Sulphur compounds are virulent poisons for nickel catalysts but in the synthesis gas purification stream the methanation catalyst is protected by the LT shift catalyst in the preceding stage which is an efficient sulphur-guard. Therefore in normal operation the methanation catalyst is unlikely to be exposed to sulphur. The exception to this would be if the LT shift converter were partially by-passed in which instance sulphur could reach the methanation catalyst. Serious deactivation of the catalyst can occur; for example one containing about 30% NiO (before reduction) shows significant loss of activity when the sulphur content exceeds ~0.1%.

The poisons most likely to be encountered on an ammonia plant are those originating in the CO₂-removal system which precedes the methanator. Carry-over of a small amount of liquid into the methanator, which is almost inevitable, is not normally serious. Plant malfunction, however, can sometimes result in large quantities of CO₂-removal liquor being pumped over the catalyst and this can be very deleterious. Table 1 shows the effect of common CO₂ - removal liquors on methanation catalyst activity.

Table 1 Poisoning effects of CO₂ removal systems

Process	Chemicals	Effect
Benfield process	Aqueous potassium carbonate	Blocking of pores of methanation catalyst by evaporation of potassium carbonate solution
Vetrocoke process	Aqueous potassium carbonate-arsenious oxide	As Benfield. Also As ₂ O ₃ is poison - about one-half of activity is lost when As = 0.5%
Benfield DEA	Aqueous potassium carbonate plus 3 per cent diethanolamine	As Benfield. DEA is harmless
Sulphinol	Sulpholane, water, di-iso-propanolamine	Sulpholane will decompose and give sulphur poisoning
MEA, DEA	Mono- or diethanolamine in aqueous solution	No poisoning effect
Cold Rectisol	Methanol	No poisoning effect

Prediction of Catalyst Life

In the operation of a methanator, it is important to be able to estimate the remaining future useful life of a catalyst charge at any moment. The question to be answered is "should this catalyst charge be changed during the shut-down planned for x weeks time or is it good enough to last until the next shut-down planned for a year hence?". Strictly, therefore, the requirement is for a Yes/No answer rather than a precise prediction, the assumption being that changing a catalyst alone will never be the reason for a shutdown. This is reasonable because, if the cost of plant down-time is compared with the cost of a catalyst charge, it is clearly economic to change catalyst rather than to run the risk of a catalyst failure causing an additional shut-down.

Methanation converters on most ammonia plants are over-designed, both for safety reasons and as a result of increases in catalyst activity since plants were built. Consequently at the beginning of the catalyst's life most of the methanation is virtually completed in the first 25% of the bed and monitoring exit gas composition gives no information about die-off of the catalyst. Catalyst deactivation occurs normally by a poisoning mechanism and, as poisoning continues, the volume of active catalyst remaining will eventually be insufficient to meet the required duty. Although the thermodynamic exit levels of CO and CO₂ are about 10⁻⁴ ppm, in practice these are not attained because of kinetic and other limitations and the actual exit concentrations, during normal operation, are of the order of 1-2 ppm.

A technique has been devised for calculating when exit carbon oxides will exceed any given design level and hence predicting the future useful life of the catalyst charge. The method is based upon accurate measurement of the temperature profile in the bed using a moveable thermocouple or a series of fixed thermocouples. A point on the profile is selected at which conversion is nearly complete. This point can, for example, be taken as the point at which 5°F temperature rise remains; the total temperature rise across a methanator is typically 60°F. The 5°F point provides a good compromise between selecting a point near the top of the temperature rise, so that pressures and temperatures can be regarded as nearly constant for the remainder of the bed, and minimising inaccuracies in temperature measurements. Obviously, if the method is valid, any selected point will give the same result. The method also assumes that CO methanates before CO₂, which is commonly accepted (Ref 2), so that over the last part of the catalyst bed, only the completeness of CO₂ methanation need be considered.

The temperature profile obtained by means of a moveable thermocouple is of the form shown in Figure 7. For highest accuracy, the maximum possible number of readings should be made in the region of the 5°F point. Interpretation of this profile to obtain a catalyst life prediction is made graphically and the mathematical derivation of the technique appears in the Appendix. The method assumes first order reaction kinetics with respect to CO₂ (Ref 2). If the gradient of the temperature profile at the 5°F point is drawn, i.e. the tangent to the curve at this point, this is a measure of the rate of reaction at this point in the bed. If catalyst activity is assumed to be constant in the remainder of the bed, this can be used to estimate the further depth of bed required for reaction to reach any selected carbon oxides level. Design limits may be imposed by the requirement to have total CO + CO₂ low enough to avoid poisoning ammonia synthesis catalyst (e.g. CO + CO₂ < 10 ppm).² More commonly, however, the main objective is to minimise ammonium carbamate, NH₄COONH₂, in the synthesis gas loop for which a limit of CO₂ < 2 ppm appears desirable.

The last 5°F rise of temperature at the end of the bed corresponds to methanation of about 465 ppm CO₂; typically methanation of 1% CO₂ produces a temperature rise of 108°F; 1% CO produces 133°F. It can be shown (see Appendix) that an exit level of 2 ppm CO₂ corresponds to the point at which the tangent intersects a horizontal line drawn 28°F above the 5°F point. The graphical constructions are therefore as shown in Figure 8. This permits identification of the present position of the "effective end of the bed" and hence of the amount of reserve

catalyst remaining. In our experience, the "effective end of the bed" is usually located by this method as 1-1.5 ft below the point at which, within measurement accuracy, maximum temperature is attained. This figure obviously depends upon the shape of the profile, i.e. on the activity of the catalyst, and should be regarded as not more than an indication. It is then necessary to study the previous history of the charge in order to estimate the rate of profile movement and likely future useful life of the charge.

The main disadvantage of this technique is that it relies upon very accurate temperature measurement, particularly near the top of the temperature profile so that the position of the 5°F point can be established and the tangent accurately constructed. Also, the end of the bed is predicted from only kinetic considerations when, in fact, other factors may be more important. In practice, however, although this introduces some scatter into successive measurements - as does variation in duty required of the methanator - the technique has proved very satisfactory. Typical findings are represented in Figure 9 where, if the present rate of catalyst die-off continues, the end of useful catalyst life is reached when the current end of the bed reaches the actual end of the bed, in this instance after about 6 years on line.

Conclusion

In summary, therefore, we can say that methanation catalysts for these applications are very satisfactory in terms of activity, strength and stability. In the absence of detrimental mal-operations, one can expect favourable operating experience and we have demonstrated a simple and convenient method by which the future useful life of a catalyst on-line can be estimated.

Acknowledgements

We are pleased to acknowledge our indebtedness to colleagues Dr P J Baldock and Mr A Parker for the X-ray crystallographic studies, to Dr P Snowden who devised the life prediction technique and to Imperial Chemical Industries Ltd. for permission to publish this paper.

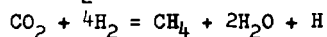
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Appendix

Derivation of Graphical Method

The CO₂ methanation reaction is:-



where H = heat of reaction

The rate of conversion of CO₂ in a short section of the catalyst bed of length dl can be calculated from the first order rate equation:-

$$dX = k_o p P^a \left[1 - f\left(\frac{K}{K_p}\right) \right] e^{-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_o} \right)} \dots \dots \dots 1)$$

where dX = moles CO₂ converted per second per unit volume of bed

k_o = rate constant at T_o
 p = partial pressure of CO_2
 P = total pressure
 T = temperature of section of bed, °K
 a = total pressure coefficient
 K_p = equilibrium constant for the reaction
 $K = \frac{(p_{CH_4})(p_{H_2O})^2}{p(P_{H_2})^4}$

Since the system is far from equilibrium, (the actual CO_2 concentration even at the exit of the bed is about 2 ppm compared with an equilibrium concentration of 10^{-4} ppm), K is small compared with K_p and the term $\left[1 - f\left(\frac{K}{K_p}\right)\right]$ becomes unity

i.e. the effect of the reverse reaction can be ignored. Equation (1) then becomes:-

$$dX = k_o p P^a e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)} \dots \dots \dots 2)$$

Considering the small section of bed of length dl and cross-sectional area A :-

Heat from reaction = $dX \cdot HA \cdot dl$ cals/second

Therefore the temperature rise dT across the section of bed is given by:-

$$dT = \frac{dX \cdot HA \cdot dl}{GC} \dots \dots \dots 3)$$

where G = gas flow rate in moles/second

C = specific heat of gas per mole at T and P

Rearranging (3) and combining with (2):-

$$dX = \frac{C}{H} \frac{G}{A} \frac{dT}{dl} = k_o p P^a e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}$$

The temperature gradient at a point in the bed where the temperature is T is therefore:-

$$\frac{dT}{dl} = \frac{HA}{CG} \cdot k_o P^a p e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}$$

Now for a point A near the top of the profile (see Fig 8) at temperature T_1 , the temperature gradient $\left(\frac{dT}{dl}\right)_1$ is given by:-

$$\left(\frac{dT}{dl}\right)_1 = \left(\frac{HA}{CG}\right)_1 k_o P_1^a p_1 e^{-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_o}\right)}$$

Now substituting for k_o in equation (2),

$$dX = \left(\frac{dT}{dl}\right)_1 \left(\frac{CG}{HA}\right)_1 \frac{P^a p e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)}}{P_1^a p_1 e^{-\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T_o}\right)}}$$

Considering only the last section of the bed where little conversion occurs, several simplifications can be made. The total pressure is virtually constant and $P_1 = P$

$$\text{Hence, } dX = \left(\frac{dT}{dl}\right)_1 \left(\frac{CG}{HA}\right)_1 \frac{P}{P_1} e^{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)} \dots \dots \dots 4)$$

The temperature change is also small so that the exponential term can be taken as unity. The molar flow, G , can be assumed to be constant between A and B and the CO_2 conversion is proportional to the change of CO_2 partial pressure, dp . The volume of the section of bed is Adl so that the rate of CO_2 conversion, dX , is therefore:-

$$dX = \frac{G}{Adl} \cdot \frac{dp}{P}$$

Combining this with (4), after simplification:-

$$\frac{dp}{P} = \left(\frac{dT}{dl}\right)_1 \cdot \frac{C}{H} \cdot \frac{P}{P_1} \cdot dl$$

Integrating between A and C, we obtain

$$\ln \frac{P_2}{P_1} = \left(\frac{dT}{dl}\right)_1 \cdot \frac{C}{H} \cdot \frac{P}{P_1} (L_2 - L_1) \dots \dots \dots 5)$$

where P_2 = partial pressure of CO_2 at bed depth L_2

For a typical methanation system,

$$C = 4 \times 10^{-3} \text{ k cal/mole } ^\circ\text{F}$$

$$H = -41.9 \text{ k cal/mole}$$

$$P = 30 \text{ at}$$

Taking A as the point 5°F below maximum temperature, at this point, 465 ppm CO_2 remains to be methanated. Take design exit CO_2 concentration as 2 ppm. Equation (5) reduces to:-

$$2.303 \log_{10} \left(\frac{2}{465}\right) = -\left(\frac{dT}{dl}\right)_1 \times \frac{4 \times 10^{-3}}{41.9} \times \frac{1}{465 \times 10^{-6}} (L_2 - L_1)$$

$$(L_2 - L_1) = \frac{28.0}{\left(\frac{dT}{dl}\right)_1}$$

$$\text{Since } \left(\frac{dT}{dl}\right)_1 = \frac{T_2 - T_1}{L_2 - L_1}$$

$$T_2 - T_1 = 28.0 ^\circ\text{F}$$

Hence a line drawn 28°F above the 5°F point will intersect the tangent to the profile at the 5°F point at the position corresponding to the present end of the catalyst bed.

FIGURE 1. D.T.A. CURVES OF BASIC CARBONATES

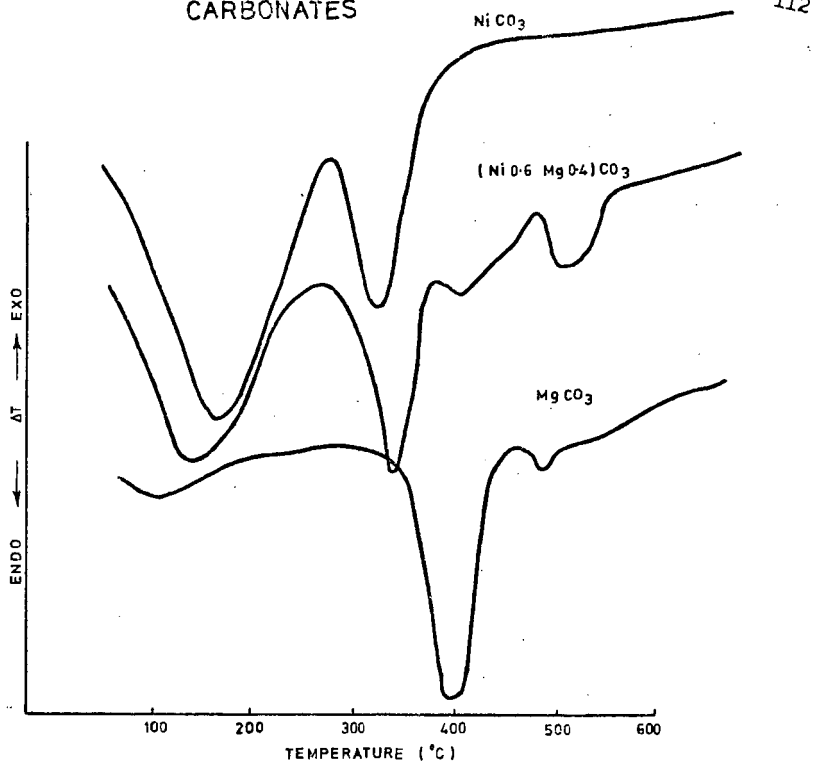


FIGURE 2. VARIATION OF CRYSTALLITE SIZE WITH CALCINATION TEMPERATURE

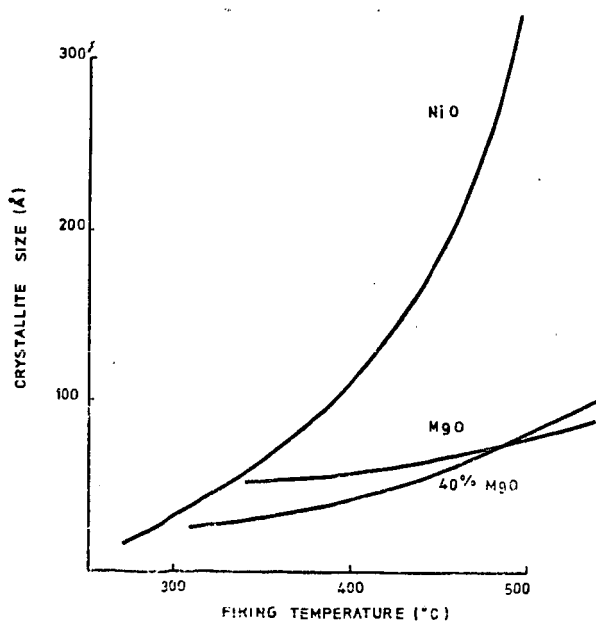


FIGURE 4. VARIATION OF NiO-40% MgO CRYSTALLITE SIZE WITH TIME

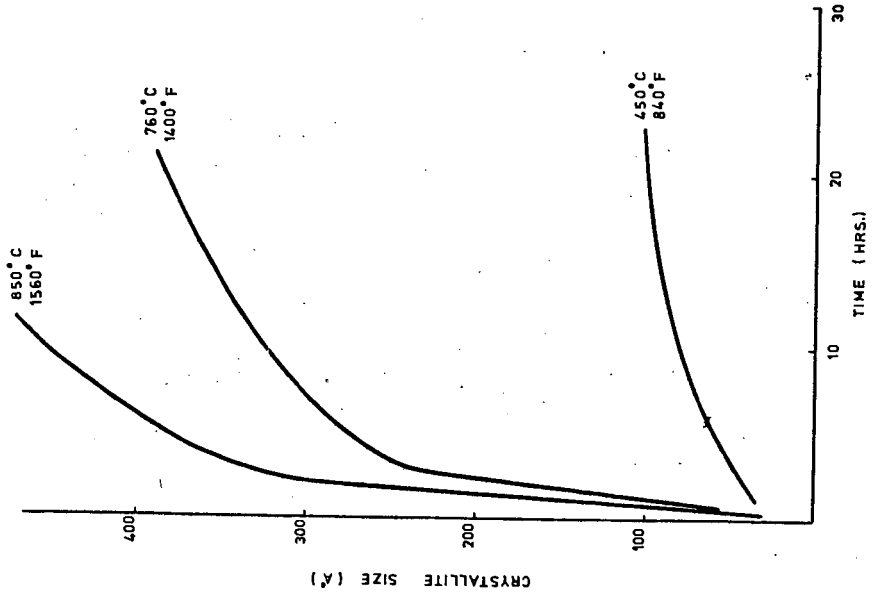


FIGURE 3. VARIATION OF NiO CRYSTALLITE SIZE WITH TIME

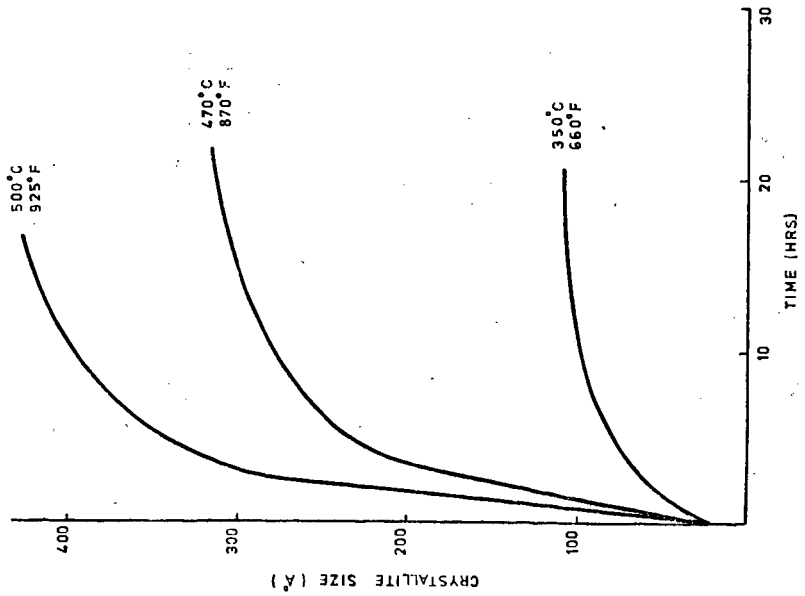


FIGURE 5. ACTIVITY vs CALCINATION TEMPERATURE

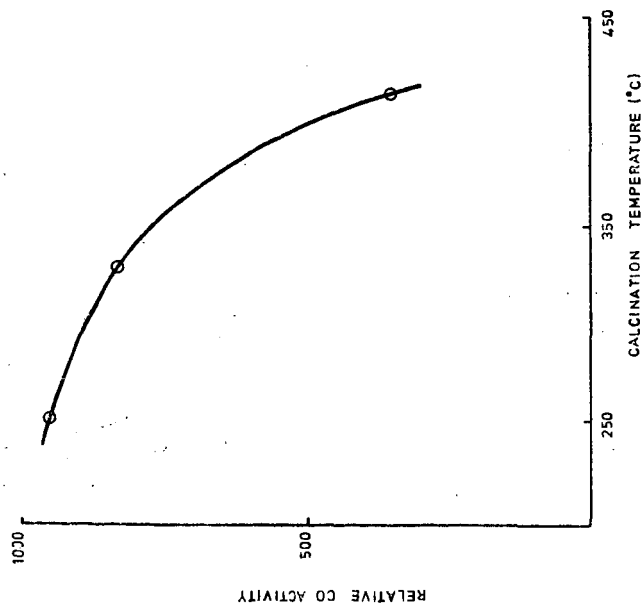


FIGURE 6. ACTIVITY vs REDUCTION TEMPERATURE

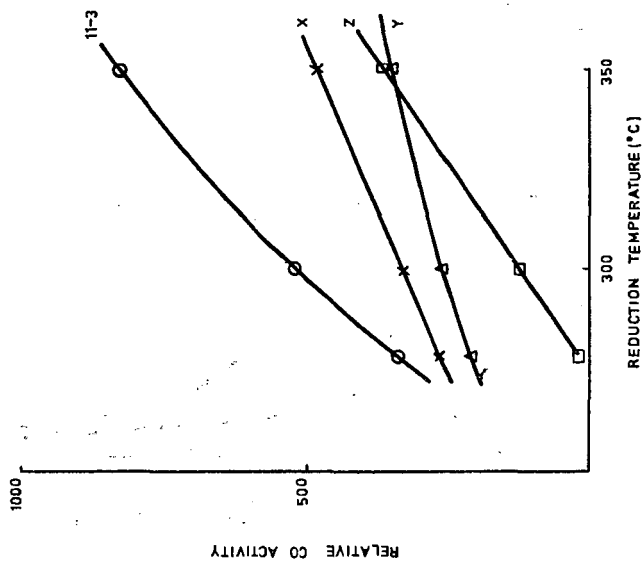


FIGURE 7. TYPICAL METHANATOR TEMPERATURE PROFILE

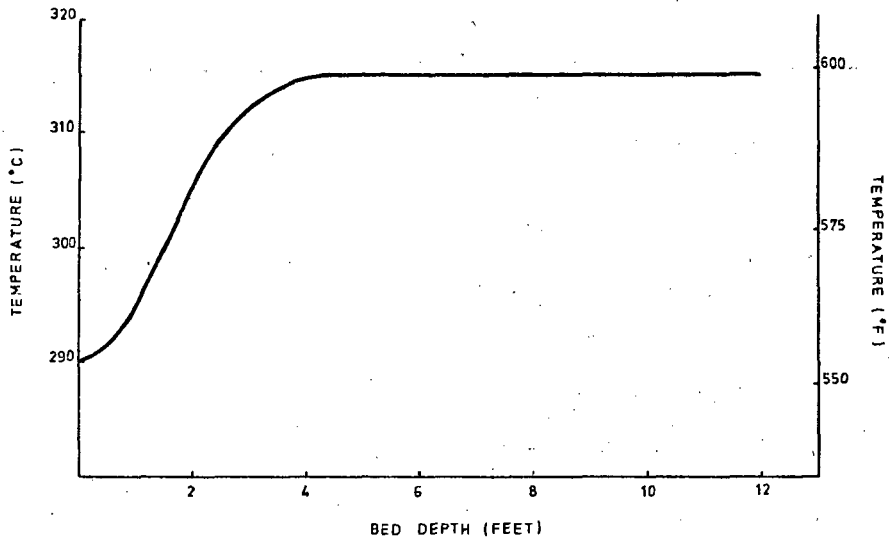


FIGURE 8. LOCATION OF EFFECTIVE END OF BED

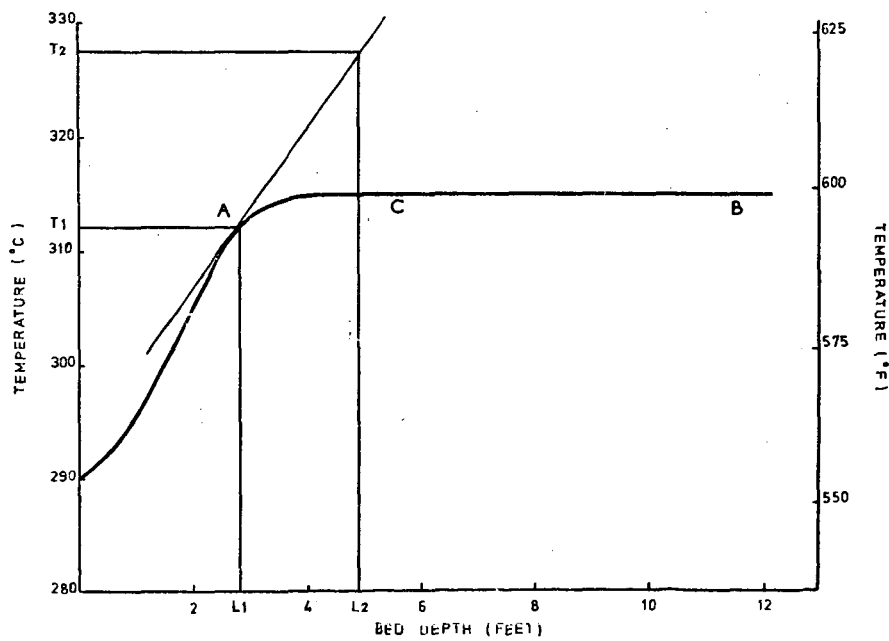
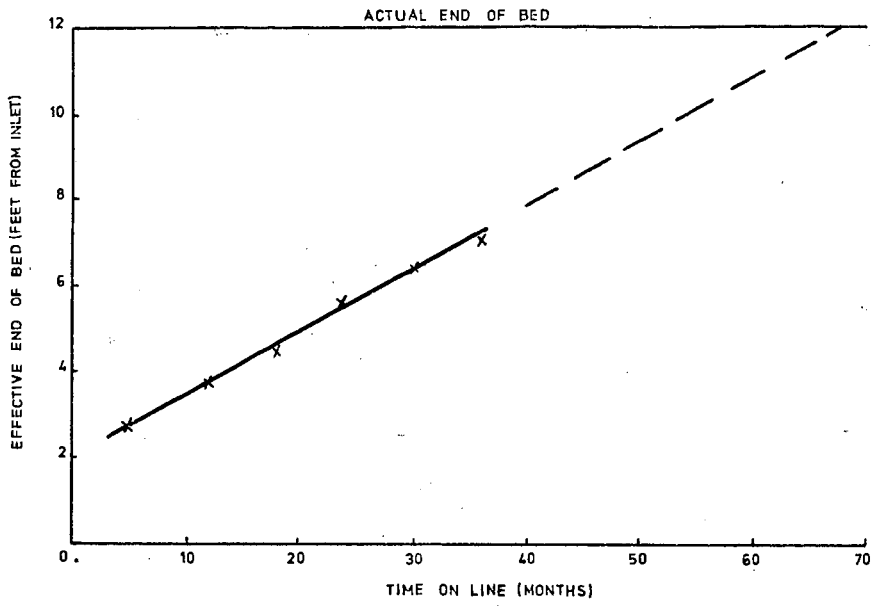


FIGURE 9. FUTURE USEFUL LIFE PREDICTION



Equilibrium Considerations in the Methane Synthesis System

Gerald Gruber

FMC Corporation, Princeton, N. J.

Summary

An investigation was made into the equilibria of the methanation reaction, coupled with the shift reaction and the carbon deposition reaction. Of particular interest is the exploration of regions where carbon deposition is possible according to thermodynamic criterion, assuming that carbon is deposited as graphite or "Dent" carbon.

The carbon laydown curves are plotted on a unique coordinate system which corresponds to starting composition variables that are commonly used. The effects of pressure, temperature and starting composition on carbon laydown are investigated over a wide range of practical interest, and beyond. All possible starting compositions are considered over a temperature range of 600°K (625°F) to 2000°K (3140°F) and a pressure range of 30 atm (426 psig) to 300 atm (4395 psig). In addition, the effects of pressure, temperature and starting composition on equilibrium composition and product gas heating value are examined. The figures presented provide a useful tool for the rapid scanning of the effect of possible starting gas composition, pressure and temperature on product gas quality and useful operating regions. The utility of the graphs are not limited to a single stage reaction, but can be used for multiple stage reactors with arbitrary amounts of diluents (H_2O , CO_2 , CH_4) and recycle gas, which may change from stage to stage. Additionally, the pressure and temperature of each stage may be considered independently.

Equilibrium Considerations in the Methane Synthesis System

Gerald Gruber

FMC Corp., Princeton, N. J.

Introduction

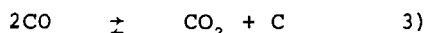
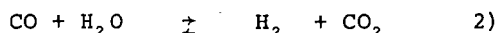
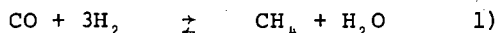
Considering the synthesis of methane from carbon monoxide and hydrogen, it is desired to operate a reactor, or reactors, in such a way as to avoid the deposition of carbon on catalyst surfaces and to produce a high quality product gas. Since gas compositions entering the reactor may vary considerably because of the use of diluents and recycle gas in a technical operation, it is desirable to estimate the effects of initial gas composition on the subsequent operation. Pressure and temperature are additional parameters.

It is a simple enough matter to calculate the equilibrium composition for any given starting composition, pressure and temperature. It is no more difficult to do it for a range of starting compositions, pressures and temperatures, except that it takes longer. Since the calculations are done on a computer, many parameters can be closely examined. However, faced with the great mass of calculated results, it is important to have them presented in a concise, informative manner.

By using a particular type of triangular diagram, it is possible to represent all possible starting compositions of CO, CO₂, H₂, H₂O and CH₄ on a single coordinate system which is easy to use.

Chemistry

Consider the following reactions which are sufficient to describe the system:



In addition, it will be convenient to make reference to another reaction:



which is not independent of reactions 1-3.

Reactions 1 and 3 are highly exothermic and therefore have equilibrium constants that decrease rapidly with temperature. Reaction 2 is moderately exothermic, and consequently its equilibrium constant shows a moderate decrease with temperature. Reaction 4 is moderately endothermic and its equilibrium constant increases with increasing temperature.

The relationship between temperature and equilibrium constant for these four reactions is indicated in Figure I, where carbon is assumed to be graphite. Thermodynamic data were taken from JANEF (1) and Rossini (2).

If we allow for the fact that carbon may be deposited in a form other than graphite, the equilibrium constants of reactions 3 and 4 must reflect the different state. This behavior has in fact been observed by Dent (3).

Dent and his coworkers found that the observed equilibrium constant for reaction 3 was less than the theoretical equilibrium constant for deposition of graphite based on measurements made between 600°K and 1200°K. The departure was greatest at 600°K, and the observed and theoretical equilibrium constants approached each other as the temperature increased, becoming equal at about 1100°K to 1200°K. The difference in free energy between graphite and the actual form of carbon deposited was also determined by decomposing pure CH_4 and by depositing carbon from a CO and H_2 mixture. These results confirmed the measurements made by decomposing pure CO . These experiments were performed over a nickel catalyst and it is speculated that the anomalous free energy of the deposited carbon may be due to the fact that it forms a carbide or a solid solution.

Whatever the exact form of the carbon deposition is, it must be recognized and taken into account in future calculations. The deposited material is called "Dent" carbon, and equilibrium constants based on its free energy are also indicated in Figure I. The fact that carbon deposits as "Dent" carbon has been qualitatively confirmed by Pursley (4).

Other recent equilibrium calculations (5, 6, 7) found in the literature assume carbon deposition to be in the form of graphite. In this paper, calculations are based on both cases, graphite and "Dent" carbon.

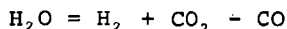
Calculation of Carbon Deposition

If we consider the system consisting of the six species, CO , H_2 , H_2O , CO_2 , CH_4 , and C , together with the three independent reactions 1 through 3, the system can be uniquely defined by specifying three species. As a matter of convenience, we

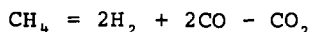
select the three species to be H_2 , CO , and CO_2 , and furthermore, by normalizing the composition such that the number of moles of the species sums to unity we only have to specify two species explicitly, which are chosen to be H_2 and CO . Then, the composition of CO_2 is implied. In order to calculate carbon deposition, for any given starting temperature the procedure is to solve equations 1 and 2 for the equilibrium composition, ignoring carbon deposition. After the equilibrium composition is obtained, a check is made to see if the ratio $(CO)^2/CO_2$ according to equation 3 would lead to carbon deposition. If no carbon deposition is indicated, then the entire calculation is repeated using equations 1 to 3 if it is desired to calculate the amount of carbon deposited. By using the above procedure, a line is defined which defines the coordinate region into two areas; one where graphite may deposit, and one where graphite may not deposit - based on equilibrium calculations. A sample of this type of graph is shown in Figure II.

Coordinate Systems

Before we discuss the curves in Figure II, a short discussion of the coordinate system will be presented. As indicated above, any possible composition of CO , CO_2 , H_2 , H_2O , and CH_4 (solid carbon also) may be depicted on the coordinate system shown if the independent species are selected to be H_2 , CO and CO_2 . Further, the sum of the species is set to unity and only H_2 (Y coordinate) and CO (X coordinate) are explicitly plotted. Pure H_2 is indicated as the point (0, 1.0) and pure CO is indicated at the point (1.0, 0). Similarly, pure CO_2 is at the point (0, 0), and compositions corresponding to pure H_2O (-1, 1) and pure CH_4 (2/3, 2/3) are also indicated. Water, for example, in terms of the independent species is expressed as



as the point on the graph corresponds to $X = 1$ and $Y = 1$. Similarly, CH_4 may be expressed as



The total number of moles is 3 so that upon normalizing $Y = 2/3$ and $X = 2/3$. In general, for a mixture of arbitrary composition, the coordinates are given by

$$Y = \frac{H_2O + H_2 + 2CH_4}{H_2O + H_2 + CO_2 + CO + 3CH_4} \quad 5)$$

$$X = \frac{CO - H_2O + 2CH_4}{H_2O + H_2 + CO_2 + CO + 3CH_4} \quad 6)$$

Furthermore, compositions may be found graphically by a lever rule. All mixtures of pure CO_2 and pure H_2 fall along the Y axis, the distance from pure CO_2 being inversely proportional to the amount of pure CO_2 in the mixture. Similar rules hold for any pair of pure components or, in fact, for any pair of mixtures, with the exception of methane, or mixtures containing methane. Since one mole of methane is equivalent to 3 moles of independent species, methane concentrations must be weighed by a factor of three.

Generally speaking, the area of physical reality corresponds to the region bounded by the straight lines connecting the pure components on Figure II. The region formed to the right of CH_4 - CO line and below the extension of the H_2O - CH_4 line corresponds to mixtures of CH_4 , CO and solid C, and, although physically realizable, is not considered here.

The two curves shown in Figure II divide the graph into graphite forming and non-graphite forming regions. These curves are for 30 atm pressure and for 650°K and 750°K , conditions which are typical of many proposed methanation processes (4, 8, 9, 10). The region below and to the right of the curve is where graphite might be deposited.

Consider the point A on Figure II corresponding to a stoichiometric mixture of H_2 and CO. If pure CO_2 is added to the mixture, the point C may be reached by moving along the line connecting the point and pure CO_2 . Similarly, if pure H_2O is added, the composition moves along the line connecting point C and pure H_2O until the point D is reached. Point B can be reached by adding H_2 and removing H_2O , which point incidentally corresponds to a stoichiometric mixture of H_2 and CO_2 , or it may be viewed as a stoichiometric mixture of H_2 and CO with an excess of water.

Suppose a starting mixture corresponding to point A, is allowed to react according to equation 1 to produce some CH_4 and H_2O . The composition of this new mixture is still represented by point A. If water is now removed from the mixture, the composition moves along the line connecting point A and pure H_2O to a point E. The extension of this line intersects the point for pure CH_4 . If the mixture, whose composition is represented by E, is allowed to react further, and if the water produced is subsequently removed, the point representing the composition will move along the line A - E getting closer to pure CH_4 .

One objective is to approach pure methane without causing the deposition of carbon or graphite, and these curves provide a rapid picture of how this may be done by operating at different starting compositions and temperatures, even with multiple stages.

Let us now focus attention on the curves in Figure II. Either one will serve as a basis for a qualitative discussion. Consider first mixtures of pure CO and CO_2 , all points of which lie on the X axis. The equilibrium in this system is fully described by equation 3. As the temperature increases, the equilibrium constant decreases, and CO becomes stable. At the temperature considered here, the mixture will deposit graphite until almost pure CO_2 is reached. Thus the graphite deposition curve will intersect the X axis at a point which is very close to $X = 0$ (at 750°K it is approximately $X = .01$). Pure CO_2 is stable with respect to carbon deposition, as is pure H_2 , but there is a large composition range where mixtures of H_2 and CO_2 will deposit graphite. Thus the carbon deposition curve intersects the Y axis at two points, as indicated on Figure II. In the region of pure CH_4 , the equilibrium is governed by equation 4. For this reaction, the equilibrium constant increases with temperature so that at high enough temperatures there will be appreciable dissociation CH_4 to H_2 and graphite. In the temperature range considered here, the thermodynamic equilibrium indicates only a very small amount of dissociation so the intersection of the graphite deposition curve and the $\text{H}_2 - \text{CH}_4$ line occurs at almost pure CH_4 . As the temperature increases, the point of intersection will move towards pure H_2 on the $\text{H}_2 - \text{CH}_4$ line.

So far, we have discussed graphite deposition only in terms of the two reactions 3 and 4. As the temperature increases, graphite deposition by reaction 4 is favored, and is retarded by reaction 3. The net result is that the graphite deposition curves for two temperatures will intersect at some point. This will become clearer when we consider curves at different temperatures than indicated here.

Carbon and Graphite Deposition

A. Pressure

In Figure II, curves for two temperatures have been presented that indicate the areas of graphite deposition. Before we consider the effects of higher temperatures, the effect of pressure will be examined.

Figure III shows the graphite deposition curves for 3 pressures at 700°K . This graph uses the same coordinate system, but is plotted on a larger scale. Again we start by considering the effects of pressure on the two, 2-component systems represented by reaction 3 in one case, and by reaction 4 in the other case.

An increase in pressure favors the reverse of reaction 4 which has the effect of decreasing the graphite formation area in the vicinity of pure methane. Thus the intersection of the graphite deposition curve and the pure $H_2 - CH_4$ line moves toward pure CH_4 . In considering reaction 3, an increase in pressure enhances the deposition of graphite and the intersection of the graphite deposition curve and the X axis will move closer to pure CO_2 . This behavior again leads to an intersection of the graphite deposition curve for two different pressures. For the temperature indicated ($700^\circ K$), the effect of pressure on the location of the graphite deposition curve is not large, although the effect is more pronounced at higher temperatures.

B. Temperature

Attention will now be focused on the effect of temperature on the graphite deposition curve, considering a larger temperature range and the deposition of "Dent" carbon.

Figure IV shows the graphite deposition curves for the temperature range of $650^\circ K$ to $2000^\circ K$. The upper temperature is far above the maximum capability of catalysts which are being proposed to carry out the methanation reaction on a large scale (6); however, it is interesting to carry out the calculations to these high temperatures, assuming that no other reactions will take place.

The behavior previously discussed is now more evident. Along the X axis, as the temperature increases, the intersection of the graphite deposition curve moves towards pure CO , while along the $H_2 - CH_4$ line the intersection moves towards pure H_2 . Thus, the odd result appears that as the temperature increases, graphite deposition is less likely for starting mixtures which are near stoichiometric, but it is more difficult to produce pure methane by removing water and reacting the mixture further. Due to equilibrium considerations, the final approach to pure methane must be done at a relatively low temperature.

If it is assumed that the solid deposit is not graphite, but has the thermodynamic properties of "Dent" carbon, the situation is quite a bit different. At lower temperatures considered, "Dent" carbon is much less likely to be deposited than graphite, as indicated by the curve for $600^\circ K$ in Figure V. As the temperature increases, the behavior of "Dent" carbon approaches that of graphite, and the carbon deposition region becomes greater. At approximately $1100^\circ K$, the curves for "Dent" carbon and graphite are the same. At higher temperatures, it is assumed that "Dent" carbon and graphite also behave identically in regards to deposition.

Since the effects of temperature on reactions 3 and 4 are in opposite directions, the different temperature curves also intersect, as is the case for graphite.

If it is assumed that the deposition of carbon is governed by the thermochemistry of "Dent" carbon, rather than graphite, it is obvious that there is a much greater region where deposition will not take place.

Equilibrium Compositions and Heating Value

The preceding discussion has been mostly confined to the carbon deposition curves as a function of temperature, pressure and initial composition. Also of interest, especially for methane synthesis, is the composition and heating value of the equilibrium gas mixture. It is desirable to produce a gas with a high heating value, which implies a high concentration of CH_4 , and a low concentration of the other species. Of particular interest are the concentrations of H_2 and CO as these generally are the valuable raw materials. Also, by custom it is desirable to maintain a CO concentration of less than 1 percent. The calculated heating values are reported according to the custom in the gas industry, which is based on a cubic foot at 30" Hg and 60°F, saturated with water vapor (11). Furthermore, it is calculated and reported for a CO_2 and H_2O free gas as these components may be removed from the mixture after the final chemical reaction. Concentrations of CH_4 , CO and H_2 are also reported on a $\text{CO}_2 - \text{H}_2\text{O}$ free basis.

The higher heating value is plotted on the composition coordinate in Figure VI. These curves are for 50 atm and 700°K. The contours of constant heating value increase uniformly in the direction of pure methane. These contours, of course, are very similar to the contours of CH_4 concentration, which are indicated in Figure VII, for the same conditions, 50 atm and 700°K.

Hydrogen concentration contours for 50 atm and 700°K are shown in Figure VIII. These contours indicate that there is appreciable unreacted hydrogen after equilibrium is obtained, and it is clear that multiple reaction stages are required to approach pure methane.

Carbon monoxide concentration contours are shown in Figure IX for 50 atm and 700°K. These curves indicate that the CO leakage will not be high if equilibrium is obtained if the initial composition is near the stoichiometric line.

Figure X shows the effect of temperature on higher heating value, CH_4 , H_2 , and CO concentrations for four different starting compositions, which are also indicated on Figure II. The four starting compositions are:

	Y	X	
1	.75	.25	stoichiometric
2	.8	.0	stoichiometric
3	.7	.1	hydrogen deficient
4	.8	.05	hydrogen rich

In this context, "stoichiometric" implies any composition point on the line connecting pure water and pure methane. These mixtures have an H_2/CO ratio of 3.0 and contain either excess water or methane. Thus, they are stoichiometric with respect to hydrogen and carbon monoxide according to reaction 1. Points falling below the line are deficient in hydrogen, and points above the line are hydrogen rich.

In Figure X-A and B, the heating value and methane concentration decrease as a function of temperature for all four starting compositions. Conversely, the hydrogen and carbon monoxide concentrations increase, as seen on Figures X-C and D. The CO leakage is about the same for the two stoichiometric points, but is considerably larger for the hydrogen deficient starting composition.

Figure XI shows the effect of pressure on higher heating value and equilibrium composition for the same four starting compositions indicated on Figure X, all for a temperature of 700°K . Generally, the effect of pressure decreases as the pressure increases, most of the change occurring in the region up to 200 atm. For all of the compositions, as well as the higher heating values, the curves for two stoichiometric and for the hydrogen deficient starting points are similar. A difference is noted for the starting composition which is hydrogen rich. This is more apparent on Figure XI because it is plotted on a larger scale than on Figure X.

General Discussion

Various schemes have been proposed in the literature for carrying out the methane synthesis reaction, some of which are in use (6, 12, 13, 14).

A major engineering problem is removing the large amount of heat generated during the synthesis and numerous ways of doing this have been considered. The reactor temperature may be controlled by recycling product gas, with or without the water being condensed, or by otherwise diluting the reacting mixture with an excess of any of the products or reactants. This effectively changes the overall mixture composition. In addition, the fresh feed composition is widely variable depending upon the source of the feed gas. However, the charts presented here are applicable to a gas of any composition and allow one to see immediately if the possibility of carbon deposition exists for any given temperature within the range of interest. On Figure V for example, it indicates that it is not possible to approach pure CH_4 at a high temperature without depositing carbon, and in fact, that a catalyst with a high temperature capability is not universally useful, but depends on the starting composition of the mixture. In any event, the final stage of the reaction to approach pure CH_4 must be carried out at a low temperature.

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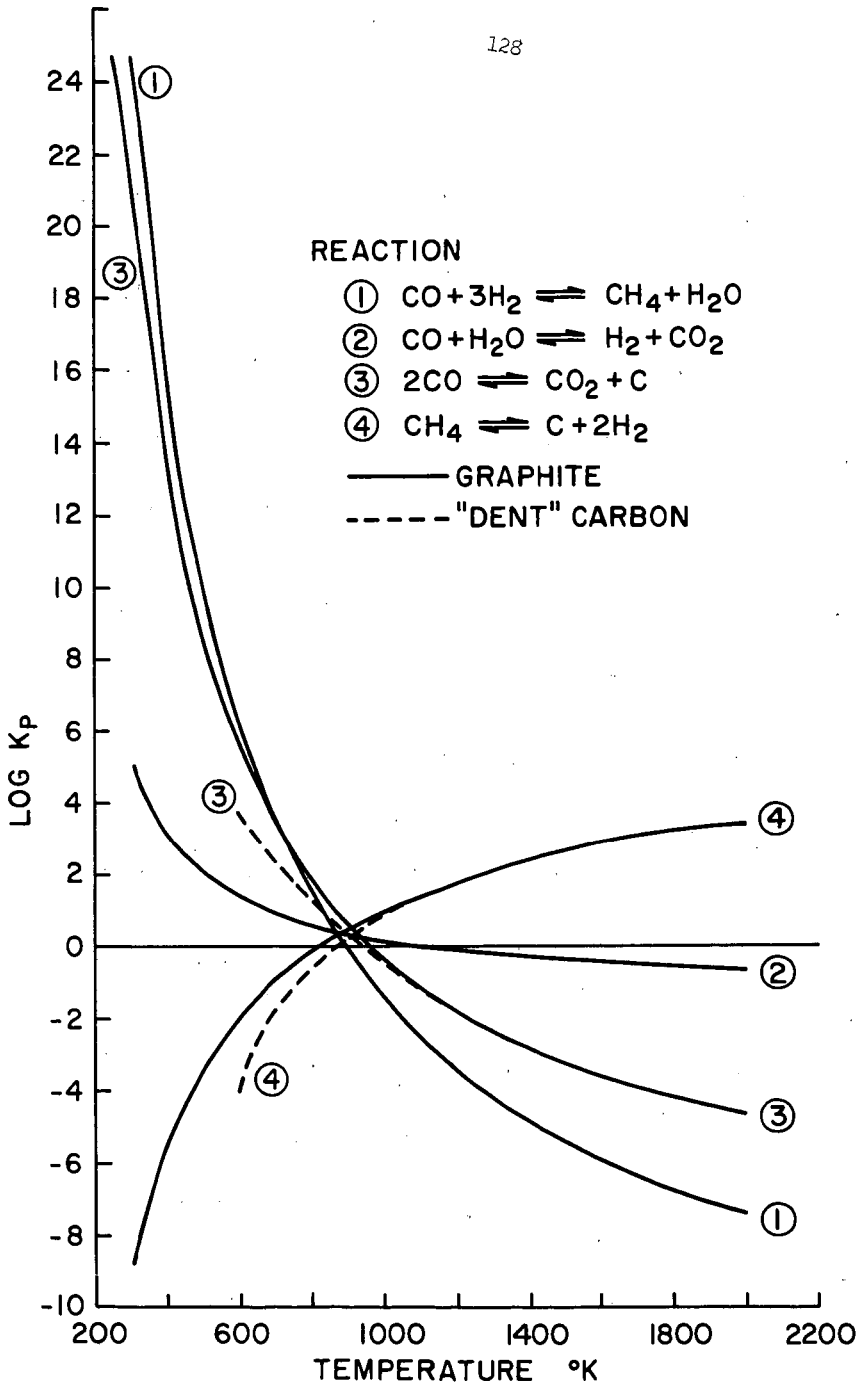


FIGURE I -EQUILIBRIUM CONSTANTS
 AS A FUNCTION OF
 TEMPERATURE

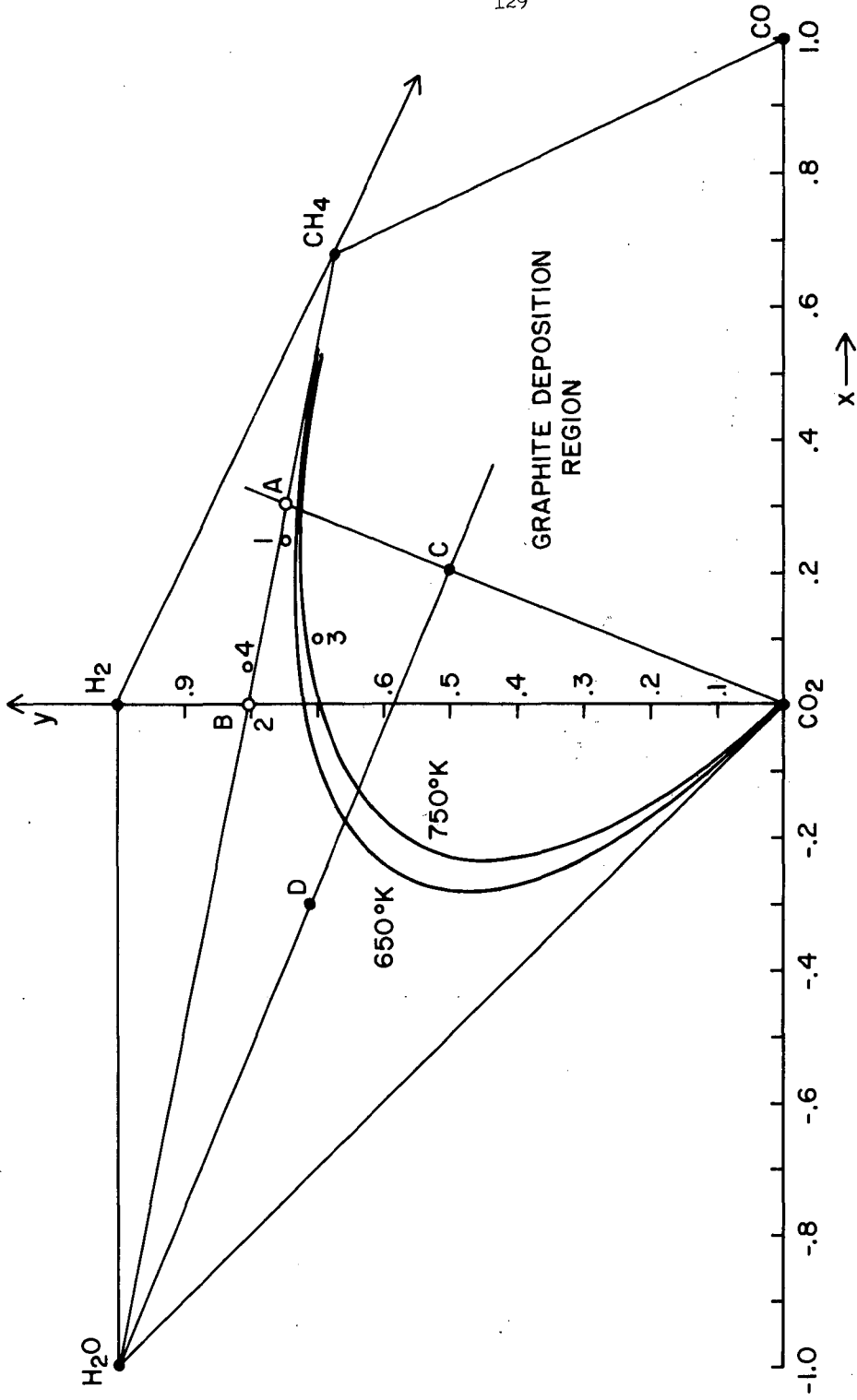


FIGURE II - GRAPHITE DEPOSITION AS A FUNCTION OF COMPOSITION AND TEMPERATURE 30 ATM

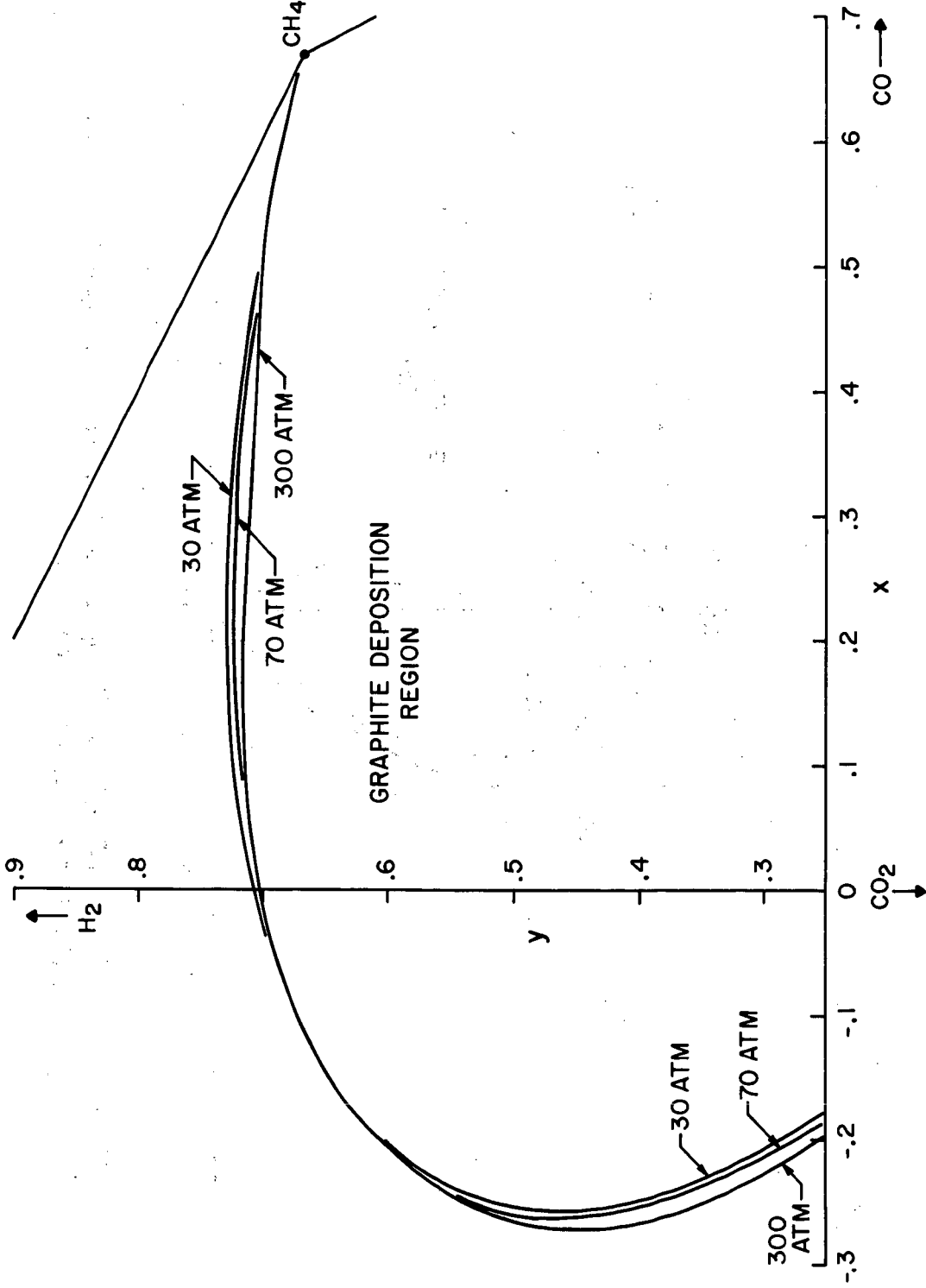


FIGURE III - EFFECT OF PRESSURE & COMPOSITION ON GRAPHITE DEPOSITION 700°K

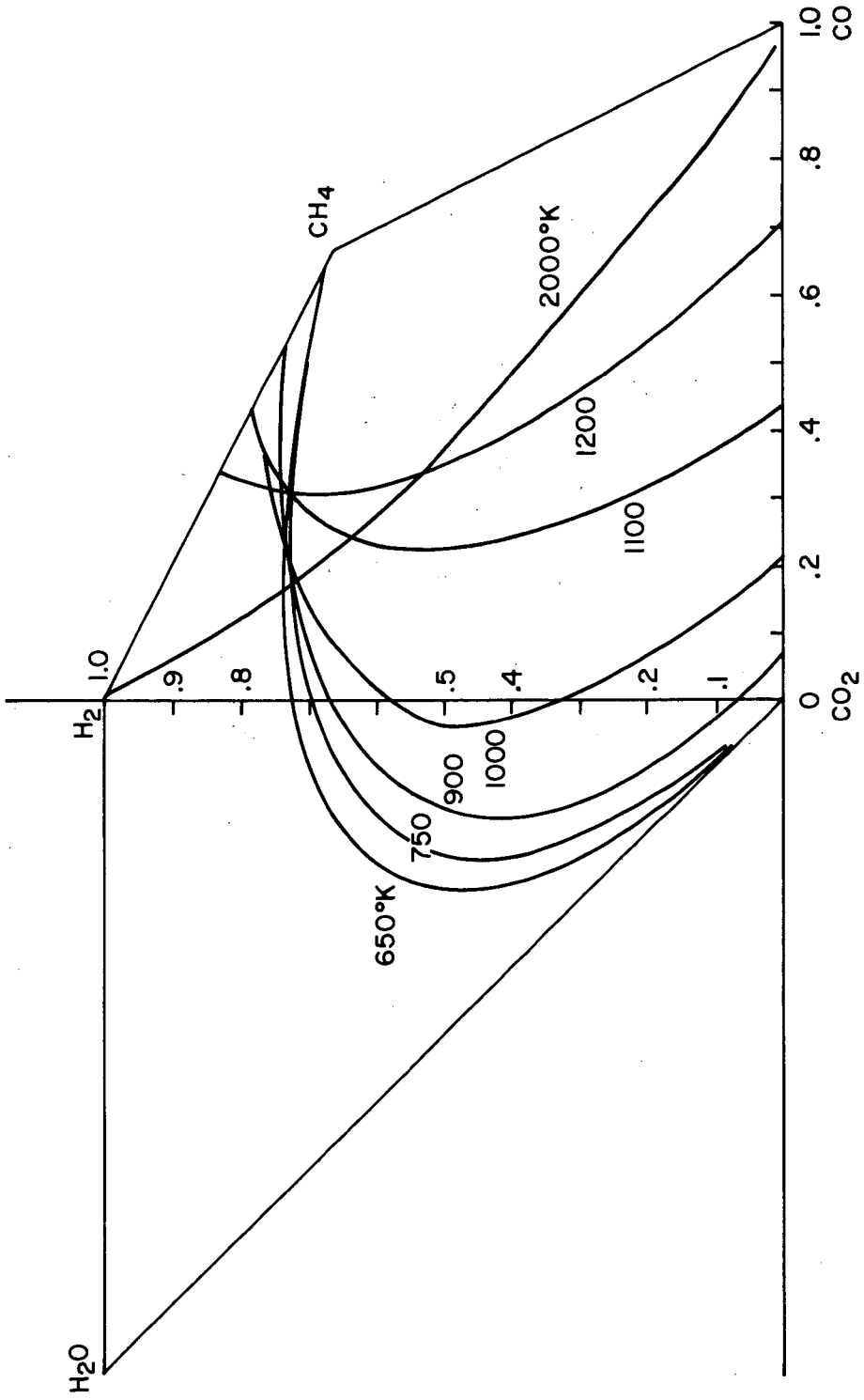


FIGURE IV - GRAPHITE DEPOSITION AT 30 ATM 650°K-2000°K

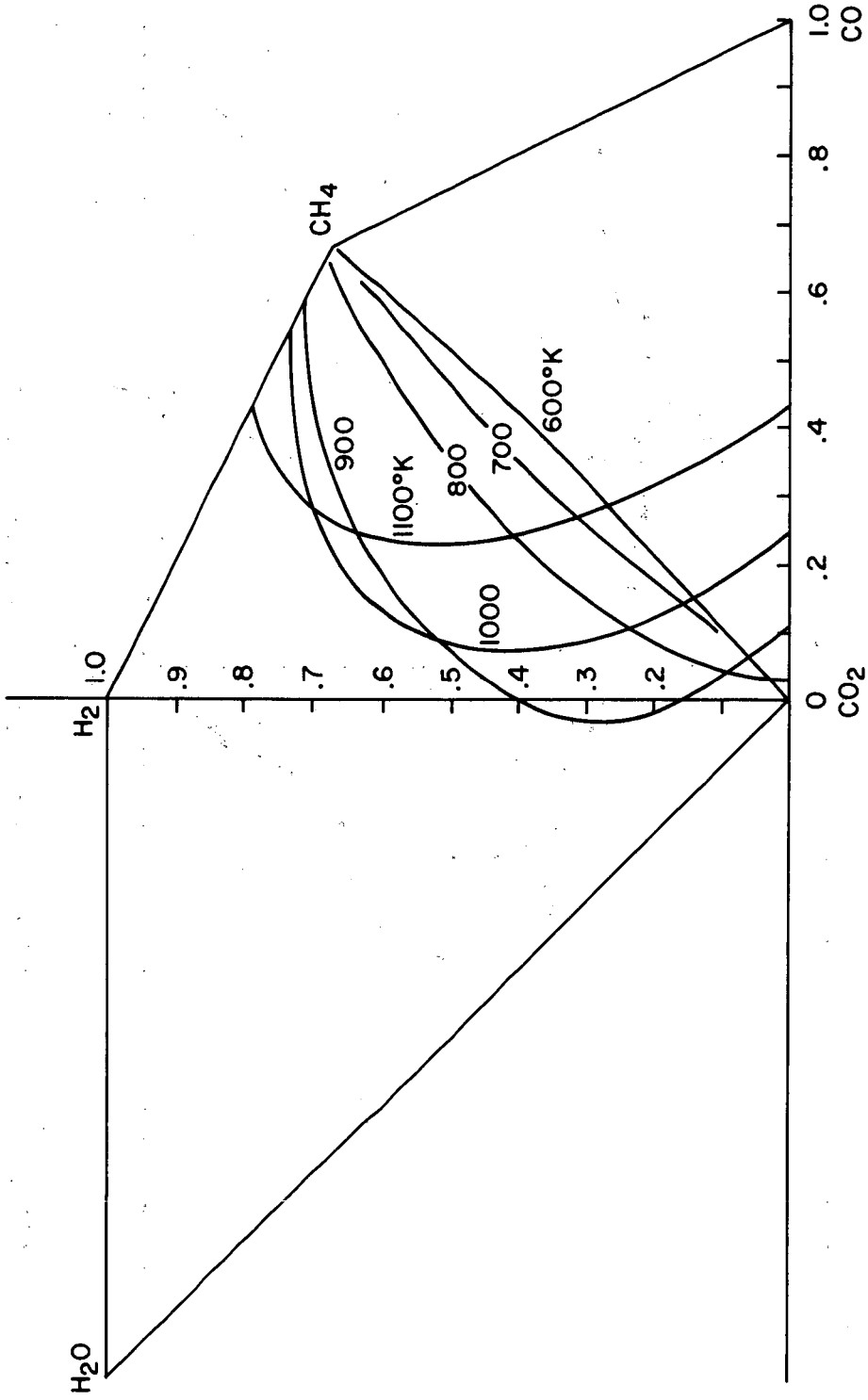


FIGURE V - DEPOSITION OF "DEND" CARBON 30 ATM

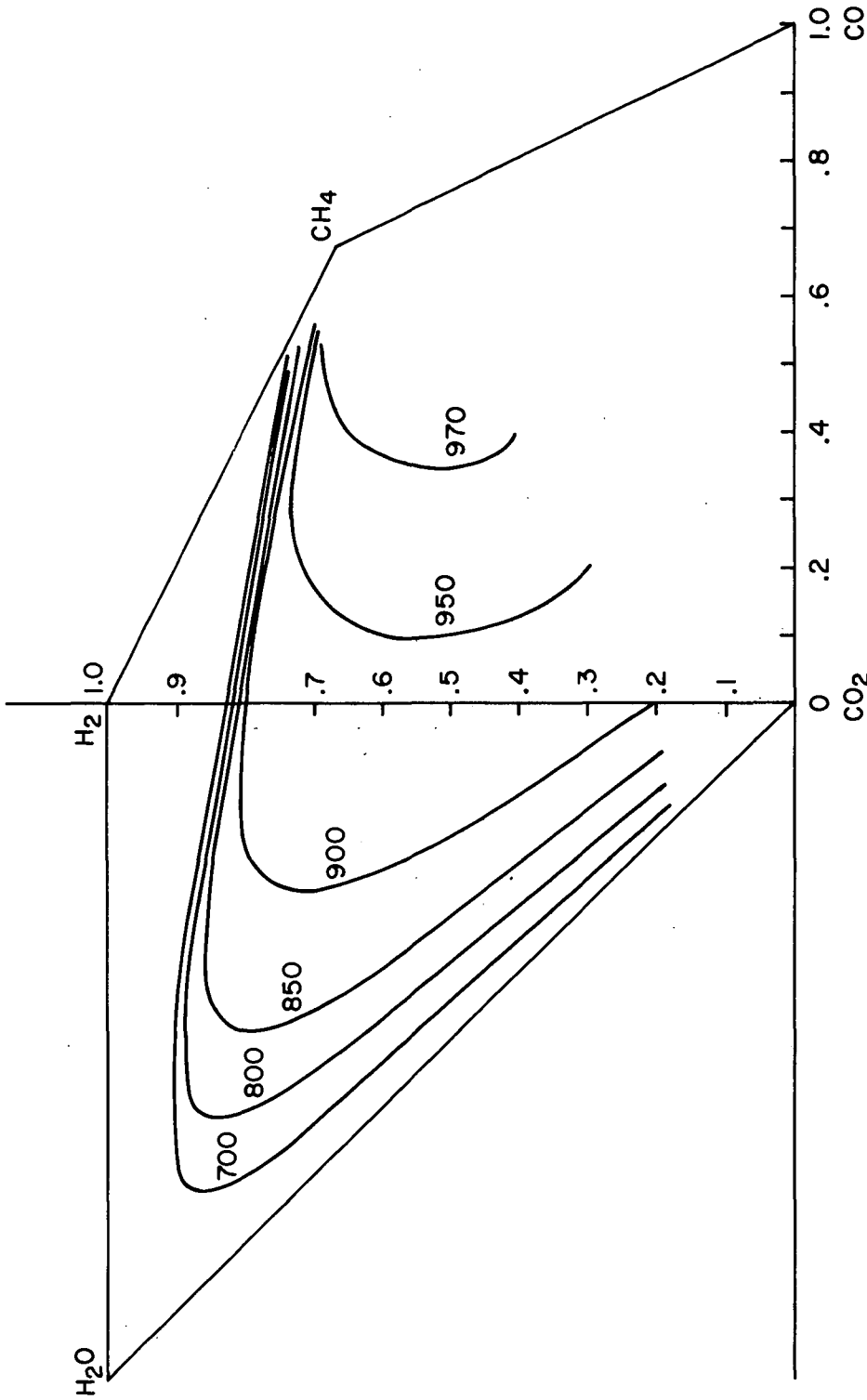


FIGURE VI - HIGHER HEATING VALUE OF CO_2 , H_2O FREE EQUILIBRIUM MIXTURES AS A FUNCTION OF STARTING COMPOSITION
50 ATM, 700°K

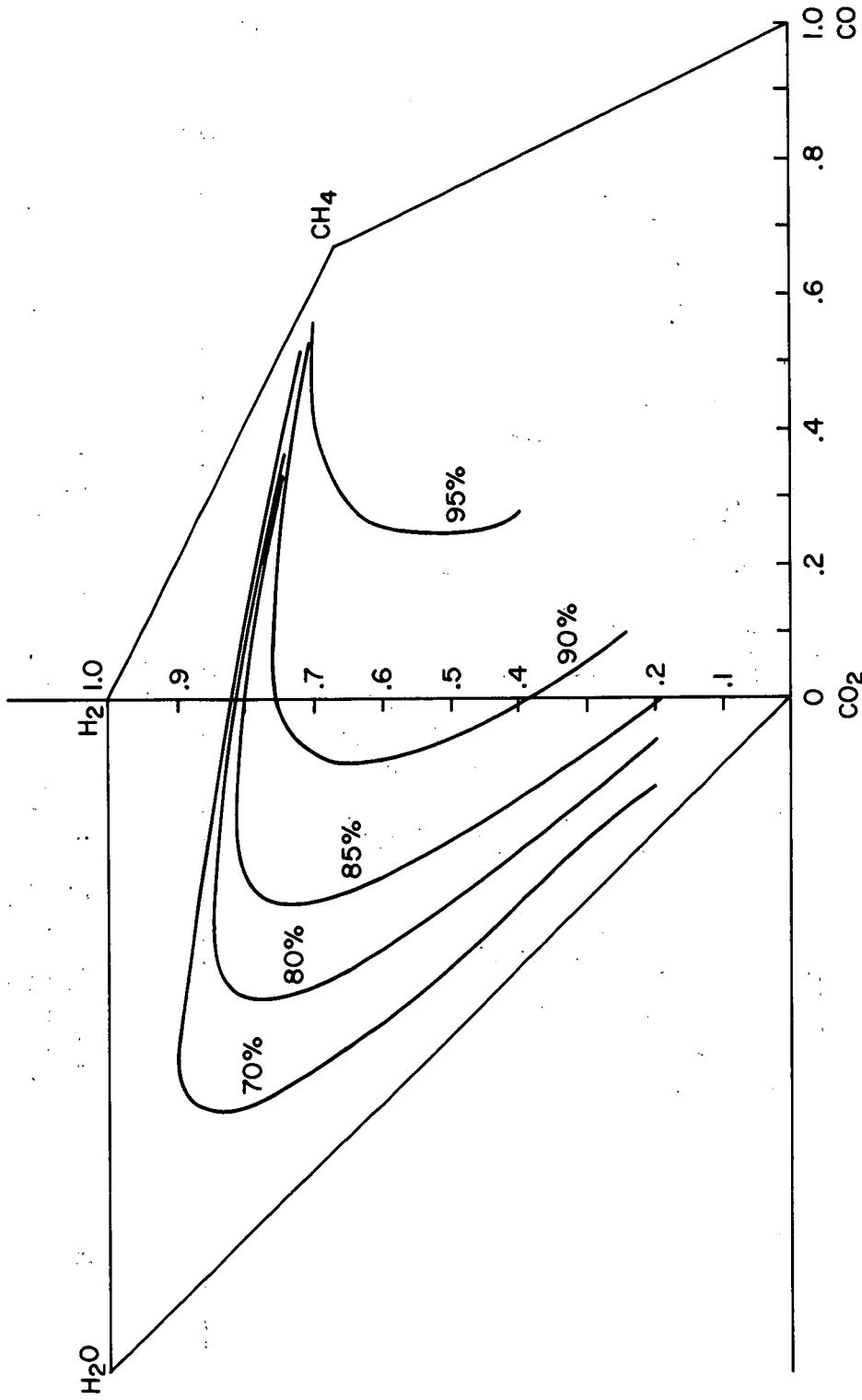


FIGURE VII - CH_4 CONCENTRATION OF EQUILIBRIUM MIXTURES
50 ATM, 700°K

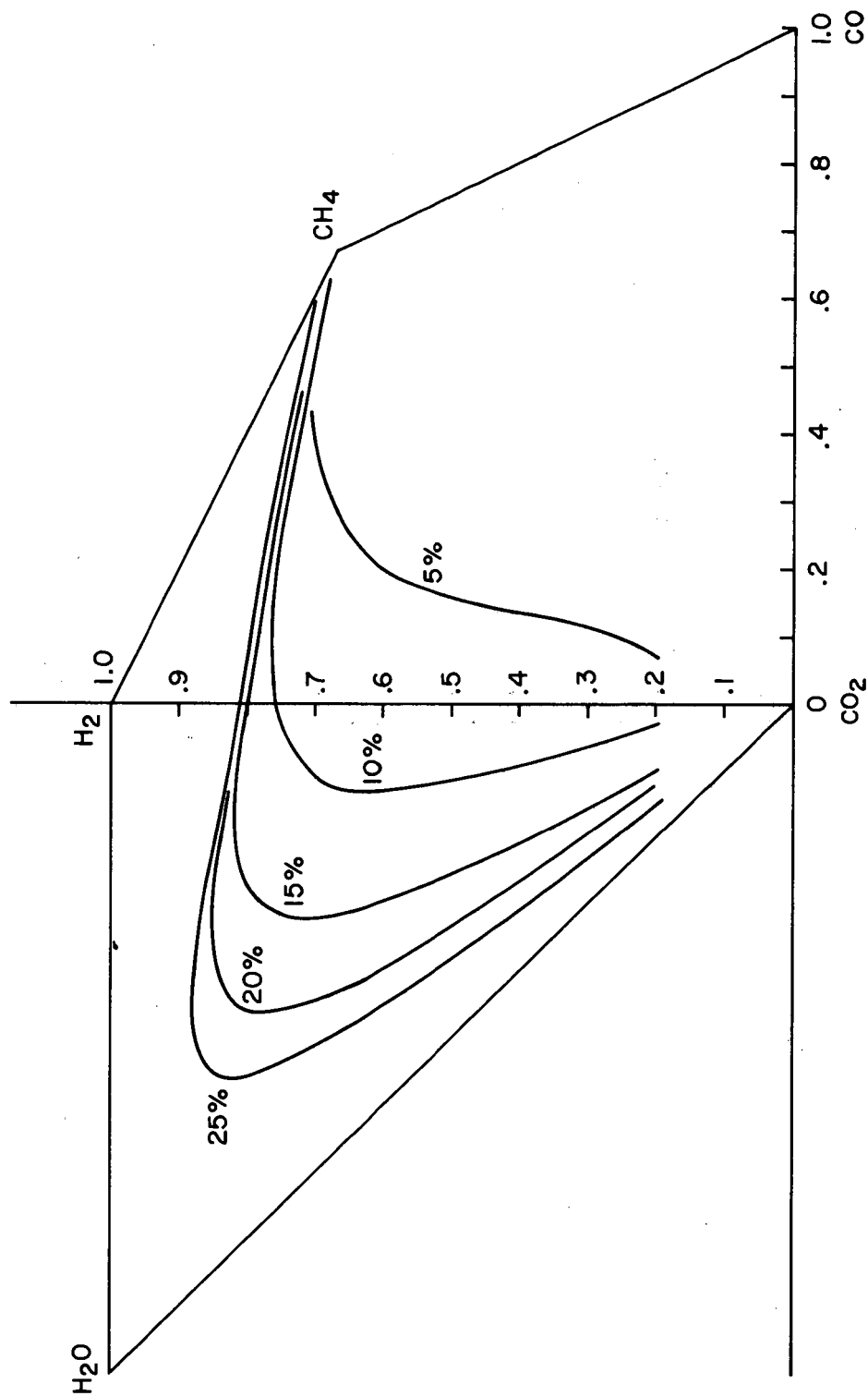


FIGURE VIII - H_2 CONCENTRATION OF EQUILIBRIUM MIXTURES
 H_2O & CO_2 FREE 50ATM, 700°K

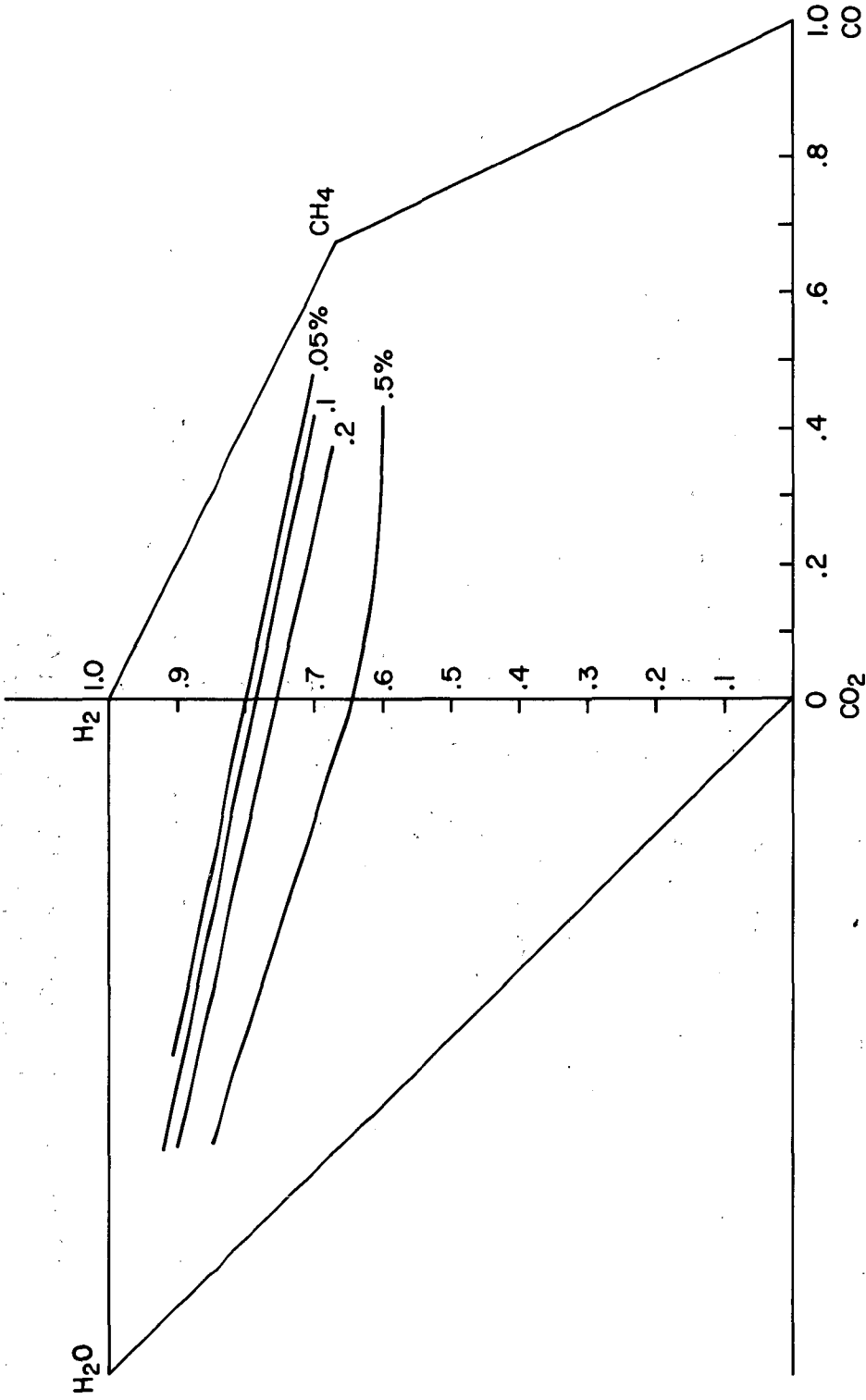


FIGURE IX - EQUILIBRIUM CO CONCENTRATION H₂O & CO₂ FREE
50 ATM, 700°K

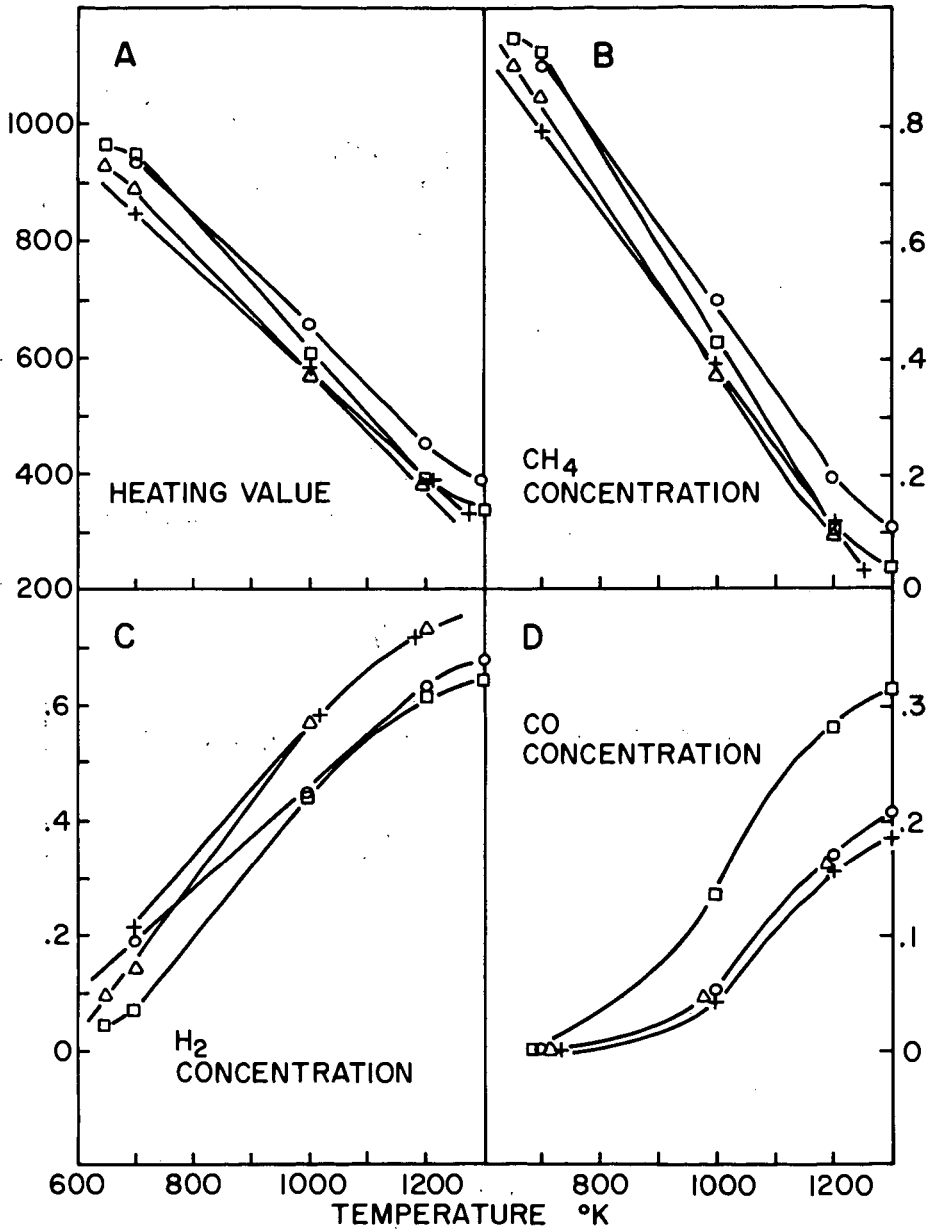


FIGURE X-EFFECT OF TEMPERATURE ON CONCENTRATION AT 50 ATM

	y	x
○	.75	.25
△	.8	0
□	.7	.1
+	.8	.05

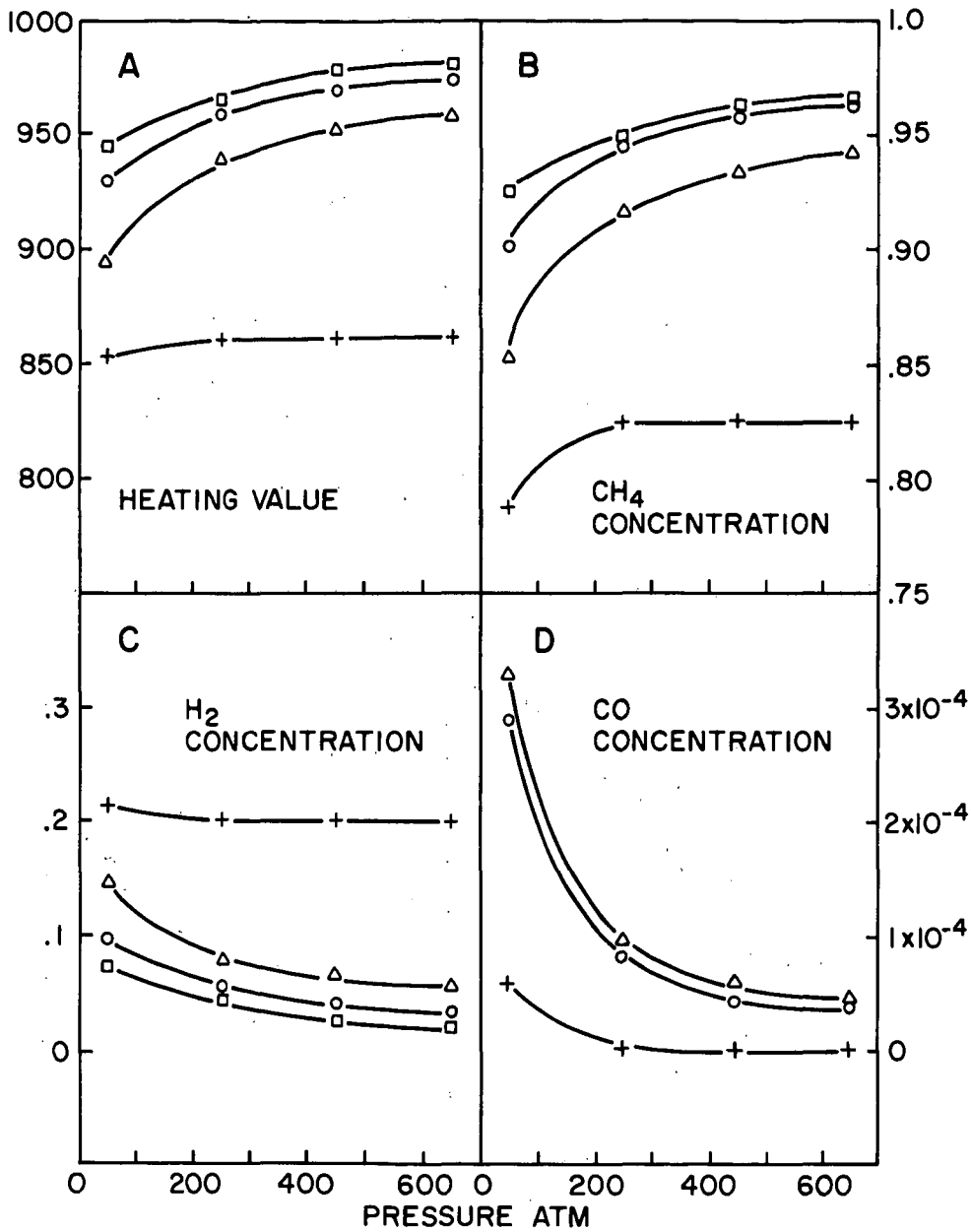


FIGURE XI-EFFECT OF PRESSURE ON
CONCENTRATION AT 700°C

	y	x
○	.75	.25
△	.8	0
□	.7	.1
+	.8	.05

MECHANISM OF THE METHANATION REACTION,

B. R. Franko-Filipasic, FMC Corporation and L. Seglin Bechtel Associates
Professional Corporation, 485 Lexington Avenue, New York, N.Y. 10017

Various mechanisms proposed for the methanation reaction are discussed, analyzed, and critiqued. Methods for testing the validity of these mechanisms are proposed, and examples are given.

FUELS 1924 - 1940

Martin A. Elliott

Texas Eastern Transmission Corporation
Houston, Texas

ABSTRACT

The period 1924-1940 may be characterized as the flowering era of fuel science and technology. In the field of combustion this period saw the extensive development of the burning of pulverized coal under slagging conditions to generate steam; a greatly improved understanding of the kinetics and mechanism of the combustion of solid fuels. Coal gasification technology was advanced: by the development of gasifiers using oxygen; by operating at elevated pressure, under slagging conditions, and with a fluidized bed; and by demonstrating the feasibility of hydrogasification. During the period the efficient by-product coke oven almost completely replaced the beehive oven for producing metallurgical coke. Coal liquefaction and solvation progressed from the laboratory to the full-scale commercial plant. The Fischer-Tropsch process was discovered just prior to the period under discussion and it too progressed to the commercial stage during this period. Major advances were made in knowledge of the kinetics and mechanism of the oxidation of gaseous fuels and in knowledge of the properties of fuel-air mixtures. Extensive work was done on the chemical constitution of coal and tar and on their physical properties. This latter work led to the establishment of many ASTM standards. These impressive accomplishments in fuel science and technology are discussed in more detail in the paper.

FUELS 1924 - 1940

Martin A. Elliott

Texas Eastern Transmission Corporation
Houston, Texas

INTRODUCTION

In discussing fuels 1924-1940 we cannot isolate this first period of the symposium from preceding developments in fuel science and technology. Accordingly, an attempt will be made to summarize, briefly, the history of the field prior to 1924. In this way we can give perspective not only to the period under discussion but also we can establish a base on which subsequent developments have been built.

The subject of fuel is so broad, covering as it does solid, liquid and gaseous fuels, that it is obvious that we will have to limit both the scope and depth of our summary.

In the period under discussion, 1924-1940, which we will refer to as "our period," the interests of the Fuel Chemistry Division followed the content of the section in Chemical Abstracts then entitled, "Fuels, Gas, Tar and Coke." This then suggests that this be the scope of our discussion insofar as the basic fuels are concerned. Thus petroleum and its products are eliminated from our discussion which is logical not only because petroleum has not been one of the basic concerns of the Division of Fuel Chemistry but also because that fuel is the basic concern of the Division of Petroleum Chemistry.

Insofar as the depth of our discussion is concerned the major emphasis will be placed on carbonization, combustion, gasification and hydrogenation. In these fields key developments will be individually referenced. No attempt will be made to document all developments by a comprehensive bibliography but rather reference will be made to pertinent books and reviews containing such bibliographies (1-6). One of these (4) contains a comprehensive list of books on fuel science and technology covering the field prior to 1943.

Obviously, to keep our discussion manageable, it was necessary to eliminate many important areas of coal research. These are covered thoroughly by Lowry (4) and include such subjects as: coal petrography; the physical properties of coals; the chemical constitution of coal as determined by reaction with various compounds; the occurrence of sulfur, nitrogen and mineral matter in coal; ash fusion; the action of solvents on coal; and changes in coal during storage. I believe it is clear that meaningful discussion could not be given to such a wide range of topics. For detailed information on developments on these and other related fields in our period Lowry's book (4) should be consulted.

BRIEF HISTORY OF FUEL SCIENCE AND TECHNOLOGY

In considering the development of fuel science and technology prior to 1924, a logical and identifiable starting point is the year 1350 when coal first became a commercial commodity. Gas was first recognized as a state of matter in 1620 and coal was first distilled in the laboratory to yield gas in 1660.

The carbonization of coal to produce metallurgical coke was known in the late 1600's but was not practiced on a large scale until 1730. Coke was a by-product of another process developed in 1792 in which coal was distilled in an iron retort to

produce illuminating gas. These two processes initially were considered basically different and this concept persisted until the early 1900's.

With the increasing use of by-product coke ovens in the early 1900's, it became apparent that it was more efficient and economical to produce gas in the by-product coke oven than in the more labor intensive gas retort. The first by-product coke ovens were constructed in France in 1856. Since then they have gradually replaced beehive ovens which in 1900 accounted for about 95% of United States production but less than 5% in the late 1930's.

In 1855 Bunsen invented the atmospheric gas burner which opened the way for gas to expand its markets from lighting to a wide range of heating applications. The need for a high illuminating power for gas was no longer required after Welsbach invented the incandescent mantle in 1884. This need would have been eliminated anyway in a few years when the incandescent electric light was invented and the gas lighting load was eventually lost.

The advent of electric lighting opened up a great potential for coal combustion in the generation of steam for power generation. Thus, the combustion of coal went through the stages of burning in open-fireplaces in the early days to burning in the fuel beds of small household furnaces and subsequently large industrial furnaces and finally to burning as pulverized fuel in large central station furnaces. This latter application was first tried in 1876 but was not successful in the United States until the factors affecting proper furnace design were elucidated in 1917.

As the use of coal gas developed, the production of gas for heating purposes was also developing. The first gas producer making low Btu gas was built in 1832. This principle was not widely used until it was applied by the Siemens brothers in connection with their invention of the open hearth furnace in 1861. The use of producer gas increased from that time, until at the turn of the century it was an important factor for heating furnaces. But subsequent to that time its use has declined and in 1920 there were only 11,000 producers in use in the United States.

Another development in the field of gas making stemmed from Fontana's discovery in 1780 of the production of blue gas when steam was passed over incandescent carbon. This discovery was dormant until the period between 1823 and 1859 when additional experimental work was done on the steam carbon reaction. This eventually led to the development of processes for producing blue water gas in the period of 1859 to 1875. The first successful commercial process was developed by Lowe in 1875 when he introduced the carburetted water gas set. The increased use of this gasification technology continued until natural gas supplanted manufactured gas.

The history of coal hydrogenation begins in 1913 when work on the Bergius concept of direct hydrogenation of coal under hydrogen pressure at an elevated temperature was undertaken in Germany. A 31 ton per day pilot plant was built in Germany in 1921 and this brings us up to our period.

The possibility of producing liquid hydrocarbons from water gas (Fischer-Tropsch synthesis) was conceived in 1913. The first experimental work on this synthesis which is sometimes referred to as the indirect hydrogenation of coal was published in 1923 just prior to the beginning of our period.

This brief review of the major areas of application of fuel technology—combustion, carbonization, gasification and hydrogenation—presents a broad picture of the status of technology prior to 1924. As each individual area is discussed more specific details of the status of significant developments will be presented.

CARBONIZATION

General

The carbonization of coal involves the interaction of a wide range of chemical and physical properties of the coal itself in a high temperature thermal environment to produce a combustible gas, hydrocarbon liquids or tar and coke. The nature of the tar and its yield as well as the physical properties and reactivity of the coke and its yield are affected by the coal used and by the carbonizing conditions. Thus an understanding of the complex coal carbonization process involves research on: the plastic, agglutinating, agglomerating and swelling properties of coals; dependence of yields of products on type of coal, temperature and rate of heating; the chemical nature of coal tar; and as stated above the physical properties and reactivity of coke.

We cannot go into detail in these areas but we will try to indicate through summaries and selected examples of some of the developments in our period. Also it is only possible to mention here such important related areas (4) as: the properties of coke-oven gas; light oil from coke-oven gas; removal of sulfur compounds and miscellaneous constituents from coke-oven gas; and the treatment of ammoniacal liquors. Finally the broad field of industrial coal carbonization can only be covered by references (2,7) which review the status of the technology up to the end of our period.

The Plastic Properties of Coal

When caking coals are heated they undergo chemical transformations during which gases and condensable vapors are evolved leaving a solid residue consisting predominantly of carbon. During this process the coal softens, becomes more or less plastic and forms a bubbly compact mass which swells and then resolidifies leaving a porous solid known as coke.

The characteristics of coal in the plastic state were studied both extensively and intensively and the results of these studies have been summarized in considerable detail by Brewer (8).

The dilatometer (9-13) which measures the variations in the length of a confined coal sample heated at a definite rate gives the most complete information on the behavior of coal in the pre-plastic range (14).

Plastometers measure the fluidity or "viscosity" of coal in the plastic range. The constant torque (Geisler) plastometer (15) gives a better index of fluidity (14) and the variable torque (Davis) plastometer (16) allows the temperature at the softening point and the resolidification point to be determined with a high degree of accuracy.

It was first shown in 1870 (17) that those coals producing the best cokes were capable of incorporating a higher admixture of inert material than those coals producing inferior cokes. This observation led eventually to the development of test methods to measure the agglutinating value of coal. The more important of these were critically reviewed in 1929 by Marshall and Bird (17) who developed an updated method for measuring the agglutinating value of coal. Their work along with that of others (18,19) led ultimately to an A.S.T.M. Standard for measuring agglutinating value.

The agglomerating properties of coal indicate the tendency of the particles to stick to one another during heating. Work on this property (21-23) led eventually to the establishment of standard methods (24,25) for determining the free swelling index which is a measure of the agglomerating characteristics of a coal.

The swelling of coal during carbonization, if excessive, can lead to serious damage to the walls of the coke oven. Much work was done in this area (8) but no standard method was developed in our period for determining this characteristic. Work by the Bureau of Mines on sole-heated ovens (26) and vertical-slot ovens (27) afforded a satisfactory means for determining the expanding properties of coal (14).

Carbonization Tests

In discussing the experimental carbonization of coals, Reynolds (14) states "A large number of assays for determining the coke- and byproduct-making properties of coal have been developed but these methods give little information concerning the quality of products because of the small amount of sample carbonized. In 1929 the Bureau of Mines, in cooperation with the American Gas Association, developed a carbonization test (28) using charges weighing up to 200 pounds. The yields of coke and byproducts from this test are large enough to be tested by standard methods, thereby affording more complete data than are obtainable from tests on a smaller scale. Forty-eight coals have been carbonized by this method at high, medium, and low temperatures, and the qualities of the cokes and byproducts determined. Petrographic, agglutinating, plastic, expanding, friability, slacking, and oxidizing properties of these coals have been studied also. The comparison of test results and plant data (available for some coals) is an important part of this work and the agreement has been close enough fully to justify confidence in the method of test. Referring to the results of these investigations, Mulcahy wrote: (29) "Although much work on coal has been regarded as too fundamental or theoretical to be of practical value, the work of the Bureau of Mines in this respect is of tremendous value in indicating the trends we can expect under different carbonizing conditions."

The subject of this section was also reviewed in detail by Davis (30).

Physical Properties and Reactivity of Coke

The physical properties of coke such as density, size, distribution and strength as determined by the shatter, tumbler and other tests are significant in relation to the use of coke in fuel beds. Work in this area for our period has been reviewed by Mayers (31).

The "reactivity" of coke is (32) "somewhat loosely used to express the ability of a coke to interact with, usually, oxygen, carbon dioxide or steam." In his review of work on reactivity for our period Mayers (31) points out that it is not necessary to determine reactivities with various agents because "By comparing series of cokes of different reactivities, it has been shown that the reactivity with air is parallel to the ignition point (33) and the reactivity to carbon dioxide (34) and steam (35) is parallel to change in the ignition point; that the reactivity to air, to oxygen, and to carbon dioxide is parallel to changes in the ignition temperature (36-38); and that reactivities to air, to oxygen, to carbon dioxide, and to steam are all parallel (39,40). In view of this no attempt will be made here to review reactivity tests. Instead certain data from such tests will be considered in connection with the discussion of gasification reactions.

Coal Tar

Coal tar is one of the primary products of coal carbonization. It is a complex mixture containing principally aromatic compounds many of which are polynuclear. In our period some 348 compounds were identified as coming from the carbonization of

coal (41). Most of these appeared in the tar. The reference just mentioned also contains information on the effect of kind of coal and carbonization temperature on the characteristics and yield of coal tar and more detailed information on certain of the individual chemical constituents of the tar.

COMBUSTION

General

Studies of the combustion of solid fuels have involved experiments: with graphite, coal and wood charcoal; with sizes ranging from less than 200 mesh particles to 1" spheres; with individual particles, clouds of particles, filaments; and with both stationary and moving fuel beds. This wide range of conditions can be considered as falling into one of two categories—basic studies and studies of combustion processes. The former includes studies with graphite in filaments or in simple geometric shapes. The latter embraces coal in the more complex systems.

Basic Studies

At the beginning of our period (1924-1940) it had already been established that CO and CO₂ were produced together (42) in the reaction of carbon with oxygen. The work of Rhead and Wheeler (43) indicated that CO was the primary product at temperatures above 1000°C. Whereas the work of Langmuir and others (44-46) involving electrically-heated filaments at low pressure indicated that CO₂ was the main product. Work toward the end of the period showed that low pressure filament results were not valid because thermions upset the initial equilibrium of the primary reaction (47). Confirmation of the results of Rhead and Wheeler resulted from high velocity experiments (48) toward the end of the period. Thus in our period we saw the resolution of the primary product of the reaction between carbon and oxygen.

According to Nicholls, (49) "the chemistry of combustion and its physics as regards to 'temperature, time and diffusion' were well understood in 1840, (50) but such knowledge was not well disseminated." In light of this it is interesting to note that early in our period it was recognized (51-53) that the rate of combustion reactions was limited by the rate at which oxygen could be transported to the reacting surface. This conclusion was supported by experimental work (54,55) on the rate of oxidation of spheres of graphite which showed (56) "that the rate of the specific surface reaction depended strongly on the temperature at low temperatures (55) but less so at high ones; (54,55) that it was directly proportional to the oxygen concentration in the gas flowing over the carbon surface; (55) that it depended on approximately the 0.4 power of the mass velocity of the gas at high temperatures; (54,55) and that, for small particles, it was approximately inversely proportional to the diameter of the particle (54). Similar effects were found for the reduction of carbon dioxide and steam (57) in work in which the monotonic effect of increasing gas velocity was used to estimate the absolute reaction rate by increasing the gas flow until no further increase in reaction rate, as measured by gas analysis, was found."

The dependence of reaction rates on gas velocity could not be accounted for by a pure diffusion process. This led to the application of the concept of the stagnant film (55,58) to account for this effect. This concept has been an important part of the development of our understanding of general heterogeneous reaction kinetics.

As discussed subsequently the extensive application of the combustion of pulverized coal in large steam boilers occurred in this period. This led to the initiation of studies of burning particles in the size range of pulverized coal.

Tests with 60 to 90-mesh particles dropped through a heated tube showed that some coal particles ignited at about 1100°F but a temperature of about 1300°F was required to ignite the major fraction of the particles (59). Later tests (60) showed that a temperature of about 1500°F was required to obtain uniform ignition of certain bituminous coals.

Combustion of individual particles of coal is complicated by the formation of cenospheres (59) as a result of simultaneous softening and evolution of volatile matter which when burned shows up as a luminous gas flame in photographic studies (59). A theoretical analysis (61) indicated that for a given quantity of excess air the burning time of a solid particle is greater than that of a cenosphere containing the same weight of combustible. The magnitude of the difference depends on the ratio of the size of the cenosphere to the size of the original particle. Burning times increase as the quantity of excess air decreases.

After reviewing basic and applied work on the combustion of pulverized coal Orning (61) concluded "Considering all the data on the mechanism and rate of combustion, it appears that a transition must occur from diffusion to surface reactivity as the controlling factor. Immediately after the zone of ignition and burning of volatile matter, the particle temperature rises very rapidly. In this region the smaller particles burn to a low carbon content within a time proportional to the square of the radius of an equivalent solid sphere and to a function depending upon the influence of coal characteristics and flame conditions upon cenosphere formation.

The larger particles will still contain a considerable portion of the total carbon after the rate of heat release has passed its peak. Continued rapid combustion of these particles depends upon their ability to maintain themselves above a certain temperature. With the combustion rate, and hence the heat release, varying as the particle diameter while the rate of loss by radiation is proportional to the surface, the largest particles will have the lowest temperature.

The reactivity of the original fuel is no indication of the temperature at which the surface reaction begins to control. The high particle temperatures in the early stages of combustion transform the residue into a material whose reactivity is mainly a function of flame conditions. The characteristics of the original fuel appear in their effect on cenosphere formation, in a possible catalysis by ash, and in a hindrance by ash incrustations.

A complete calculation of burning times must consider the possibility that the surface reaction rate will begin to control beyond a certain degree of combustion. Lack of data on the reactivity and configuration of combustion residues and the dependence of particle temperature upon an equilibrium with furnace surroundings make it inadvisable to attempt a general solution."

Combustion in Fuel Beds

Combustion in fuel beds has been reviewed by Mayers (56), Nicholls and Barkley (49), and Haslam and Russell (3). This type of combustion encompasses the open grate, the central house-heating furnace and the various types of mechanical stokers.

At the beginning of our period extensive research had already been done to improve the convenience and efficiency of the coal fire-place (62). Also extensive tests had been made by the Bureau of Mines and others (63-66) on the combustion of various coals on a grate in a cylindrical furnace. These tests provided information on the effect of rate of firing on gas composition in the fuel bed and on the temperature of the fuel bed. The tests showed conclusively that the quantity of coal burned or the capacity of

the furnace depends entirely on the quantity of primary air coming into the furnace under the grate. The Bureau of Mines also studied the combustion of gases over the fuel bed and in this instance demonstrated conclusively that the quantity, distribution and turbulence of secondary air determines the efficiency of the furnace. Thus at the beginning of the period there existed a significant body of practical knowledge on combustion in fuel beds.

During the period additional work was done on the combustion of various coals in house heating boilers, (67) on the performance of domestic anthracite stokers, (68) on the fundamentals of combustion in small underfeed stokers (69) and on burning various coals in domestic overfeed stokers (70).

Most of the work on various types of stokers during the period involved improvements in mechanical design to secure a high degree of reliability and a high conversion of fuel into heat (71-75).

Mayers (56) states that "The conditions within the beds of travelling grate stokers have been determined experimentally (76-78). These investigations show that the layer of coal entering the furnace is ignited at the top of the bed; and that the surface dividing ignited from raw coal moves down as the layer passes through the furnace. The ignition surface reaches the grate ... where the dense flame of volatile matter stops; all the fuel has been ignited and coked at this point, and only the coked residue is burned out beyond it. As this process proceeds, a larger and larger proportion of the bed becomes ash refuse. The fire should be operated so that all the fuel is burned out of the refuse short of the end of the grate, but the air quantity passing through this end of the grate must be controlled to prevent excessive losses."

Spreader stokers were a relatively new development in this period. The principles of operation are essentially similar, so far as the fuel bed is concerned, to those obtaining in hand-firing, the stoker being merely a means of producing a continuous flow of small amounts of fresh fuel down into it. Description of such units and the results of tests made on them are given by Barkley (79-80).

Combustion of Pulverized Coal

The use of pulverized coal in the firing of large steam boilers came into being at the beginning of our period. For example, the boiler heating surface fired with pulverized coal increased from 200,000 sq. ft. in 1918 to 2,000,000 sq. ft. in 1925 (44). The progress of this development throughout our period has been detailed by Orning (45), Haslam and Russell (46), and Nicholls and Barkley (49).

The early developments in pulverized coal combustion as well as developments later in our period have been summarized by Nicholls and Barkley (49) as follows:

"In 1917 a report (65) of the Bureau of Mines showed that a long travel of flame was required to give complete combustion unless the air and the combustible were mixed vigorously. When furnaces for pulverized-coal firing were so built they gave satisfactory performance and good efficiencies (81). The cooperative work of the Bureau of Mines and the Milwaukee Electric Railway and Light Co., resulted in the first successful application of pulverized fuel in the steamboiler field.

In the earlier designs successful removal of the ash required that the particles be deposited in a dry or unmolten state. These dry-bottom furnaces were not so successful with coals having low-fusion ashes. The problem was solved by going to the other extreme of maintaining the ash in a liquid state and tapping it intermittently or continuously; the wet-bottom furnace was the outcome.

Operation of these furnaces depends largely on the properties of the coal ash and its slag. As relatively few data were available, the Bureau of Mines initiated in 1929 a study on the ash factor in such furnaces and the properties of coal-ash slags in general (82)."

The initiation of the systematic study of coal-ash slags followed closely the first successful application of the slagging-type furnace (83) and the first studies on slagging conditions in full-scale furnaces (84). Other studies of conditions of temperature and gas compositions in full-scale furnaces were directed toward the explanation of the striking difference in refractory service conditions in two similar furnaces (85) and toward the effect of different burner and heat absorption configurations (86).

HYDROGENATION

Coal hydrogenation was practiced for the first time on a large scale in Germany in 1925 and subsequently in France, Great Britain, Japan and the United States (87). In commenting on these early developments Storch (88) states:

"Except for a relatively small amount of research published by the British Fuel Research Laboratory, little information on the fundamentals of coal hydrogenation is available, despite the voluminous patent literature, which is often more confusing than informative. Unquestionably much more is known by industrial interests, particularly in Germany and Great Britain, than appears in print. However, a study of the development of coal hydrogenation in these countries reveals that the intensive drive made during the past decade to achieve large-scale production has left little, if any, time and funds for fundamental research."

The literature on coal hydrogenation prior to 1931 was reviewed by Skinner and Zerbe (89,90) and between 1931 and 1938 by Fieldner (91). These reviews along with two books by Berthelot and Hot (92) and reviews by Storch (88) and Wu and Storch (87) cover the basic work on coal and tar hydrogenation in our period.

Studies of the hydrogenation of a number of British coals in small bombs showed that the yield of oil boiling below 360°C at atmospheric pressure increased approximately linearly with the carbon content of the coal. (93) As a corollary the reactivity of the coals to hydrogenation was approximately inversely proportional to their carbon content.

Similar studies on the hydrogenation of the mechanically separable constituents of American coals showed that the translucent constituents (spores, resins, oil algae, translucent attritus, and anthraxylon) are liquefied completely. The opaque constituents (fusain and opaque attritus) contain about 75 to 95 percent and 20 to 60 percent, respectively, of materials resistant to hydrogenation.

On the basis of the foregoing results, it was suggested (94-96) that "petrographic analysis would be a desirable, although only semiquantitative, tool for predicting liquefaction yield upon hydrogenation." This was confirmed by work done in the Bureau of Mines' experimental plant (97) which showed fair agreement between petrographic estimates of organic residue yield and yields obtained in the continuous operation of the plant. These tests were made on nine coals ranging in rank from lignite to bituminous A.

Laboratory work on the effect hydrogenating coal in the presence of a catalyst (stannous oxide), with and without a vehicle, showed that these two variables are not independent of each other (98,99). For example with small amounts of catalyst (less

than 0.1% of charge) the addition of a vehicle results in an appreciably greater yield of volatile products. With higher concentrations (more than 0.5%) the effect is small and may even become negative.

The extensive work done in our period on the effect of catalysts on the liquid phase hydrogenation of coal has been reviewed in considerable detail by Storch (88).

In laboratory studies, the catalytic effect of the walls of the converter cannot be neglected. (100) This effect is less important in large diameter industrial reactors although it may be of considerable importance in engineering development work involving the use of small diameter tubes (101-103).

The effect of the halogens in enhancing the activity of stannous oxide, stannous hydroxide, ammonium molybdate and nickel sesquioxide as liquid phase hydrogenation catalysts was demonstrated by the British (104,105) and Japanese (106,107). Results obtained with various catalysts on the liquid-phase hydrogenation of coal are generally applicable to the liquid-phase hydrogenation of tar (108).

The preparation and performance of catalysts for the vapor-phase hydrogenation of low temperature tar and middle oil has been discussed by Storch. (88) Information on such catalysts as supported molybdenum oxide, pelleted molybdenum or tungsten disulfide as well as on many others is also presented.

Tests on the effect of pressure on the liquid-phase hydrogenation of coal showed little effect on the capacity of a small-scale plant in the range of 180 to 250 atmospheres. (109) However, Pier (110) stated: "The conversion of old coals or of asphalts of high molecular weight, which goes but slowly at 200 to 300 atmospheres, proceeds without difficulty and at a satisfactory rate for large-scale production at considerably higher pressures, e.g., 700 atmospheres or more."

An increase in temperature in the range of 420 to 460°C increases the yield of crude gasoline, middle oil and hydrocarbon gas and decreases the yield of heavy oil (oiling of 300°C) and solid organic residue. (111,112) The hydrogen absorbed also increases with increasing temperature. The effect of temperature and contact time are analogous in that higher temperatures are equivalent to a longer contact time (111).

Storch (88) points out that "coal is usually hydrogenated for the single purpose of producing hydrocarbon fuels. Consequently, there has been little incentive to study the characteristics of intermediate products such as the "middle" oil (boiling range 210 to 330°C) from liquid-phase coal hydrogenation. As a source of organic chemicals, however, this intermediate product is most interesting and merits examination. The middle oils from liquid-phase coal hydrogenation contain benzene, toluene, xylene, cyclohexane, methyleyclohexane, about 20 percent of tar acids (phenol, cresols, xylenols), and 2 to 5 percent of nitrogen bases." In addition "several patents mention the isolation of many polynuclear aromatic compounds of high molecular weight from coal-hydrogenation products. Sometimes the actual isolation is preceded by dehydrogenation. Products of this kind include pyrene, chrysene, retene, fluoranthene, carbazole, methyl- and dimethylpyrenes, 1,12-benzoperylene, coronene, picene, fluorene, methylanthracene, and naphthalene." (88)

"The products of the hydrogenation of coal are largely aromatic and naphthenic in nature, whereas appreciable yields (about 12 percent) of the paraffin hydrocarbons have been reported in the hydrogenation of German brown coals (88)."

Tar may be hydrogenated under the same conditions as coal except that no solid materials other than a small quantity of catalyst powder in the case of high temperature tar must be introduced or removed from high-pressure vessels. Low-temperature

tar may be processed directly by mixing with recycle oil and hydrogen and passing the mixture over a fixed catalyst bed in a high-pressure vessel.

The effect of process variables on the yield and distribution of products are essentially the same as in the case of coal as shown in Storch's review (124) of tar hydrogenation covering our period. This review also shows that this similarity also exists in the nature of the products obtained from the two feedstocks.

SYNTHESIS OF HYDROCARBONS FROM MIXTURES OF CARBON MONOXIDE AND HYDROGEN

The catalytic conversion of mixtures of carbon monoxide and hydrogen to hydrocarbons which is referred to as the Fischer-Tropsch synthesis or the gas synthesis process was developed and commercialized in our period. The details of laboratory research and industrial development have been reviewed by Storch. (113) A more comprehensive treatise on the Fischer-Tropsch and related syntheses was published in 1951. (114) The vast amount of work done on the Fischer-Tropsch synthesis in Germany, Great Britain, Japan and the United States cannot be presented here. Instead, we will quote the excellent brief summary of developments in our period given in the book by Storch et al. (114)

"The Fischer-Tropsch synthesis had its origin in an observation made in 1923 by Franz Fischer and Hans Tropsch that alkalized iron turnings at 100-150 atm of hydrogen plus carbon monoxide and 400°-450°C catalyzed the production of "synthol." This product consisted chiefly of oxygenated compounds and a very small quantity of hydrocarbons. At 7 atm and, later, at 1 atm, Fischer found that the distribution of oxygenated and hydrocarbon products was reversed. The first Fischer-Tropsch catalyst was an iron-zinc oxide preparation which was reported by Fischer in 1925. It was tested at atmospheric pressure with a mixture containing 3 volumes of hydrogen and 1 volume of carbon monoxide, and at a temperature of 370°C. However, development of iron catalysts was unsuccessful until 1937, which was several years after the Fischer-Tropsch process was in commercial operation with a cobalt catalyst.

An important advance in the development of Fischer-Tropsch catalysts was the precipitation of nickel-thoria on kieselguhr in 1931. This catalyst was followed in 1932 by the corresponding cobalt catalyst, 100Co:18ThO₂:100 kieselguhr, parts by weight, which was the starting point in the development of the Ruhrchemie commercial catalyst. Subsequent changes in catalyst composition, concomitant with process development, resulted in a standard composition in 1937 of 100Co:18ThO₂:200 kieselguhr and in 1938 of 100Co:5ThO₂:8MgO:200 kieselguhr.

The advantages of iron over cobalt, in being easily available from many sources and in imparting flexibility to the process, stimulated continuous research on iron catalysts. In 1937, alkalized precipitated iron catalysts were successfully operated on a laboratory scale by the Kaiser Wilhelm Institut für Kohlenforschung at 15 atm of water gas and at temperatures of 235°-250°C.....

In the Fischer-Tropsch process as developed commercially by the Ruhrchemie A.G. in Germany in 1935-1940, synthesis gas containing 2 volumes of hydrogen per volume of carbon monoxide was compressed to about 7 atm and passed through a granular bed of cobalt catalyst at 185°-205°C. The major products of the synthesis were wax, oil, water, gaseous hydrocarbons, and a minor amount of carbon dioxide. The hydrocarbons were largely straight-chain paraffins. The olefin content varied with pressure, contact time, and temperature. Improved modifications of the Ruhrchemie process involved the recycling of exit gas from the reactor and the use of iron to replace cobalt in catalyst preparation. These changes increased the olefin content of the product and the flexibility of the process, particularly in the control of the proportions of gasoline, Diesel oil, and alcohols."

GASIFICATION

General

As in the case of combustion, research and development work on coal gasification in our period can be divided into basic studies and studies of and development of gasification processes. Work in the latter areas can be considered in three categories: (a) processes for making low-Btu or producer gas; (b) continuous processes for making intermediate heating value gas; and, (c) intermittent processes for making blue-water gas and carburetted water gas.

Basic Studies

In all gasification processes the endotherm of the steam-carbon reaction must be supplied by the combustion of some of the fuel with air or oxygen. Accordingly, the results of much of the basic work on combustion of carbon are also applicable to the gasification of carbon. However, gasification also involves the reaction of carbon dioxide with carbon and of steam with carbon.

Prior to our period considerable work had been done on the reaction of carbon dioxide with carbon to form carbon monoxide. This reaction is referred to as the "Boudouard reaction" (115) because Boudouard was the first to study its equilibrium. The reversal of the above reaction can occur in the gas space above the fuel bed and is referred to as the "Neumann reversal" (116) because Neumann was the first to direct attention to the possibility of its occurrence. The carbon dioxide-carbon reaction as well as the steam-carbon reaction were studied extensively by Clement and co-workers (117) and by Rhead and Wheeler (43,118). The former study presented data on the effect of temperature and time of contact on carbon dioxide or steam conversion. The latter study presented data on reaction rate constants and advanced the concept of a carbon surface covered with an adsorbed film of oxygen referred to as the "carbon-oxygen complex." During our period evidence was presented of the existence of the "carbon-oxygen complex" (46,119-121) and on its role in the mechanism of gasification reactions.

Basic studies of gasification prior to and during our period have been thoroughly reviewed by Mayers (56,122), Orning (61) and Haslam and Russell (3). In addition to reviewing such studies van der Hoeven (123) has reviewed developments in the production of producer gas and Morgan (124) has reviewed developments in the production of blue water gas. Work on the gasification reactions done prior to 1933 has been reviewed by Logan (125) and Elliott (126) who subsequently reviewed developments in the gasification field prior to 1940 (127).

As stated earlier (31) the reactivity of carbon to air, to oxygen, to steam and to carbon dioxide are all parallel. Therefore relative rates of reaction determined with one reactant are generally the same with one of the other of the above reactants.

Blakely and Cobb (128) studied the effect of contact time at two different temperatures on the rate of reaction of carbon dioxide with a variety of cokes and other forms of carbon and also the effect of temperature at constant time of contact. Reactivity decreased with an increase in contact time because the more reactive parts of the surfaces had already been consumed. Similar effects would be expected with steam.

In a study of the influence of coke reactivity on the formation of water gas Bunte and Giessen (35) observed that in the case of the more reactive cokes a large fraction of the steam was decomposed by the reaction forming one mole of carbon monoxide and one mole of hydrogen per mole of carbon. They pointed out that the value obtained for the quantity of steam decomposed was not characteristic of the actual conditions in

the fuel bed but was influenced by the subsequent establishment of water gas shift equilibrium in the gas phase.

P. Dolch (129) analyzed the data of Burte and Giessen (35) and of M. Dolch (130) and concluded that there is no experimental evidence that the reaction of steam with carbon to form CO_2 and hydrogen occurs but that the reaction forming CO and hydrogen with the subsequent water gas shift reaction are of primary importance. In the experiments analyzed, water gas equilibrium was obtained at a temperature of 800°C with reactive carbon materials such as lignite coke and wood charcoal. With less reactive cokes, such as gas coke, water gas equilibrium was not attained until temperatures approached 1000°C .

In earlier studies of the steam carbon reaction (131,132) the catalytic effect of ash on the water gas reaction was observed. The first studies on the magnitude of the effect of catalyzing the steam carbon reaction were made by Taylor and Neville (133) in 1921 just prior to our period. They found that potassium and sodium carbonates were the most effective catalysts of all those investigated, and they clearly demonstrated that their effect was indeed catalytic. They believed that the catalysts accelerated the decomposition of the surface complex of carbon and oxygen suggested by Rhead and Wheeler (43), thereby exposing a clean carbon surface which was reactive to carbon dioxide. Carbon dioxide produced in the water gas shift reaction would then interact with this carbon to form additional carbon monoxide which in the presence of excess steam would react as above to form additional quantities of carbon dioxide and hydrogen, thus increasing the net increase of gas from the steam-carbon reaction.

Marson and Cobb (134) found that sodium carbonate was the most effective additive in gasifying laboratory coke at 1000°C . It was found that additions of potassium carbonate and sodium sulfate were just as effective in catalyzing the steam-carbon reaction as was sodium carbonate. In this same investigation it was observed that those additives which produced a maximum effect on the steam-carbon reaction exhibited an analogous effect on the reduction of carbon dioxide by carbon.

Additives were effective in the range of concentrations from 0.5 to 5.0 percent. Sutcliffe and Cobb (135) studied the effect of temperature on coke containing %5 additives of various constituents. The accelerated effect was considerably greater at 600°C than at 1000°C . Similar studies were made by other investigators (136).

Studies of the mechanism of the catalysis of the carbon gasification reactions (136,137) showed that the acceleration is brought about by the alternate reduction and reformation of the alkali carbonate in the following manner: The sodium carbonate first reacts with carbon yielding carbon monoxide and sodium in a mol ratio 3:2. The sodium thus transported into the gaseous phase is at liberty to react with carbon dioxide with the subsequent formation of carbon monoxide and sodium oxide. The sodium oxide may then further react with carbon dioxide to form sodium carbonate which is deposited on the carbon surface and is therefore capable of further reaction.

The steam-carbon reaction may also be catalyzed when carbon is deposited on a refractory impregnated with a sodium containing salt (126).

Toward the end of our period Dent and co-workers (138) laid the foundation for the hydrogasification of coal in studies of the kinetics of methane formation in the reaction of cokes and coals with hydrogen at elevated temperatures and at pressures ranging from 1 to 100 atmospheres.

Producer Gas

Studies of the reactions occurring in the fuel bed of a gas producer have been made by several investigators (3,139). The zones designated (3) from top to bottom are: ash zone; oxidation zone; primary reduction in which the steam-carbon and carbon-dioxide-carbon reactions occur; the secondary reduction zone in which the water gas shift and carbon dioxide reduction reactions occur; distillation zone in which the volatile matter in the fuel is added to the gas; and finally the gas space in which a decrease in heating value may occur as a result of the so-called "Neumann reversal" of the Boudouard reaction.

The effect of steam in the air blast of a producer was well known prior to our period (140). Additional work was done in our period (141,142) and it was established that the efficiency of the producer reached a maximum between 0.3 and 0.4 lbs. of steam per lb. of coal. However this range may have to be exceeded in practice to avoid clinker formation.

Work on the performance of full-scale producers done during our period was summarized (3,123). The latter reference discusses a variety of theoretical, thermodynamic and stoichiometric analyses of the producer gas process.

Development work on the slagging gas producer was done prior to our period (123). Data from tests on these producers (123,143) made in our period and on some of their further developments and operating characteristics were described (144).

Continuous Production of Intermediate Heating Value Gas

The use of oxygen in the blast of a producer was advocated (145-147) just prior to the beginning of our period. Experimental work (148) done first at atmospheric pressure led eventually to the development of the Lurgi process which operated at 20 atmospheres. Data on the effect of pressure in increasing the heating value of gas from the Lurgi process was presented by Hubmann (149) and Danulat (150).

The Lurgi process was commercialized in 1936 and made possible the continuous production of gas having a heating value as high as 450 Btu per cu. ft.

The Winkler generator which used oxygen or oxygen-enriched air and steam to gasify lignite or semi coke was developed and used commercially in our period (150,151). In this process a fluidized bed was used for the first time in gasifying solid fuel.

Carbureted Water Gas

The production of carbureted water gas reached a peak in 1926 (124) when it represented about 60 percent of the total manufactured gas in the United States. To put this into perspective, the energy in this quantity of gas represents about 0.5 percent of the energy in the natural gas produced in 1973. Today (1974) carbureted water gas is not being produced in the United States. In view of this, developments in our period will be mentioned only briefly. These have been discussed (124,127) and include the application of automatic controls; the use of mechanical grates; the substitution of heavy oil for gas oil; the application of the back-run process; reforming of refinery and natural gas in water gas generators; and, the production of high-Btu gas that could be mixed with or even substituted for natural gas.

SUMMARY

In the period 1924-1940 we saw many developments in fuel science and technology that were innovative and of lasting importance. Methods for classifying coals and their petrographic constituents were developed. Tests for determining the properties of coals and cokes were in many instances standardized. In the United States a standard method for carbonizing coal was developing to determine yields of coke, gas and tar and to evaluate the utility of these products.

In the field of combustion we advanced our understanding of the basic combustion reactions and of combustion of coal in fuel beds as well as in pulverized form. This latter development is up to the present time the most widely applied advance of any in our period.

In the area of gasification we also advanced our understanding of basic gasification reactions. But most importantly we saw many innovations such as the use of oxygen; gasification at elevated pressures; the use of fluidized beds in gasification reactors; the direct gasification of coal and coke with hydrogen; and the improvement of slagging gasifiers.

The period 1924-1940 saw the development and commercialization of technology for producing liquid fuels directly from coal and indirectly by the catalytic conversion of carbon monoxide and hydrogen produced from coal. Commercial synthetic liquid fuel plants were important to Germany in World War II but such processes are not generally economical today. However modifications of this technology may be economic in the near future.

The advances in gasification and production of synthetic hydrocarbons have not as yet had a major impact on the field of energy conversion but they most certainly will in the future.

It is apparent that the period 1924-1940 was most productive in developing fuel science and technology that has given us energy conversion technology that has made possible the widespread use of coal and other fuels in the generation of electricity today. In the emerging era of producing synthetic gaseous and liquid hydrocarbons from fossil fuels we will certainly draw heavily on the advances in gasification and hydrogenation made in the 1924-1940 period. Let us hope that the next 50 years of research and development on fuel science and technology and on other sources of energy will be as productive of useful technology as the first part of the past 50-year period.

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FUEL CHEMISTRY 1940-1960

by

H. R. Batchelder
Harlan W. Nelson

I. INTRODUCTION

During the period 1940-1960, the study of fuel chemistry was subject to a serious perturbation that persisted for 6-8 years (1945-53), after which research in this field essentially resumed its previous pattern. Dr. Fieldner gave an excellent review of this field in his paper for the ACS Golden Anniversary.

Up to the end of World War II, those doing research in fuel chemistry were concerned to a large extent with coal. The ranking of various coals, the determination of its components, the study of the properties of these components and especially attempts to elucidate the structure of the coal substance were some of the major subjects covered. The elucidation of the coal structure was investigated by studying the products found when various coals or coal fractions were subjected to a fairly wide variety of chemical reagents or treatments.

Those concerned with the utilization of coal were looking primarily for ways to convert it to a smokeless fuel (or at least reduce smoke formation), for ways to determine its coking properties, for ways to use blends as a means of producing a better coke for metallurgical uses, and for ways to reduce the amount of premium medium-volatile coals used so as to use a greater proportion of the less expensive high-volatile coals. The behavior of various coals under the influence of heat and pressure were studied in the laboratory and in a number of experimental ovens. The gas, oil, tar, and pitch resulting from carbonizations were examined and processes were developed for separation of many important chemical products.

The bulk of the research on coal was carried out by a relatively small number of organizations, almost all falling into three classes: the U. S. Bureau of Mines, several of the Schools of Mineral Industry in various universities, and a number of State Geological Surveys or Bureaus of Mineral Industries. This research partook substantially of an academic nature - the research people were in search of knowledge primarily for its own sake, but always with the hope that this knowledge would prove useful in the future.

The large consumers of coke did their research on carbonization primarily in order to develop more efficient, economical processes or to produce a more desirable end product.

The above do not by any means cover the full range of interests of the Fuels Division, but an examination of past programs shows that these subjects were predominant.

Toward the end of World War II, with its shortages and rationing and the expectation of "taking up where we left off", serious concern regarding the country's petroleum futures emerged. It was this situation which gave rise to the perturbation.

To show briefly the situation, Figure 1 shows the U. S. oil proven reserves and production during the years 1935-1944. The reduced rate of discovery and the then fantastic increase in consumption led to serious concern about our oil futures and resulted in the passage of the Synthetic Liquid Fuels Act. For a few years the interests of the Division of Fuel Chemistry were sharply focussed on the problems of producing gasoline from coal and from oil shale.

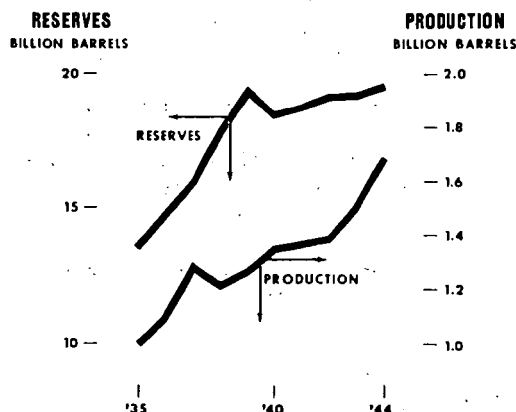


FIGURE 1. CRUDE PRODUCTION AND RESERVES, 1935-1944

Looking back over the programs of the Division meetings, between 1940 and 1960 we find a sharp rise (in many cases from none at all) in papers on coal hydrogenation, coal gasification, coal reactions, and Fischer-Tropsch synthesis. The emphasis was all on liquid fuels; no one thought of natural gas, except as a potential source of hydrogen for coal hydrogenation.

Institutions previously engaged in coal research promptly shifted the emphasis in their work toward the solution of what was generally regarded

as a most pressing problem. In addition, there began to appear papers whose authors worked for companies whose future was tied closely to petroleum or to products made therefrom.

The emphasis in research again shifted with the later advent of the Middle East oil at prices that were extremely attractive, and with the estimated reserves in the Middle East that seemed almost unlimited. Interest in liquid fuels from coal subsided very rapidly, the Office of Synthetic Fuels was eliminated, and many of the academic research workers (or their successors) returned to the study of coal as a substance - looking for an increase in knowledge that would contribute in the future to the advancement of science.

Rarely, if ever, has such a severe dislocation in a field of research been experienced, and rarely has interest in a particular area of science and technology disappeared so rapidly.

This is the period that we will attempt to explore. We will concentrate to some extent on the production of liquid fuels from coal, partly because it caused the perturbation and partly because of its present interest.

In order to supply some background we will review the fuels situation worldwide and in the U. S. during the period 1940-1960.

Because of its importance at the time and because of its relevance today we devote a fair amount of time to the production of synthetic liquids from coal, and the production of synthesis gas and hydrogen, also from coal. From some years these occupied the attention of many of those concerned with coal chemistry.

The history of the demise of that effort and a brief summary of the situation in 1960 will complete our story.

II. REVIEW OF FUELS SITUATION - 1940-1960

In the United States in 1940, there was little reason for concern regarding domestic energy sources. Coal, petroleum, and natural gas (locally) were all in abundant supply. Reserves, if considered at all, were judged to be ample for the foreseeable future. As a matter of fact, one concern was the persistent displacement of coal as a source of energy by petroleum and its derivatives and the consequent reduction of coal mining. Much natural gas was being flared or used for the production of carbon black, and the by-products were wasted to the air.

The distribution of our various sources of energy is shown in Figure 2 from 1940 to 1960. At the beginning of the period, coal supplied about half of our needs, but lost ground steadily; first to petroleum then after the advent of gas pipelines, to natural gas. By 1960 coal was supplying only about one-fourth of our energy needs. These needs had increased significantly during the postwar years. Petroleum, whose situation was so disturbing during the immediate postwar years had increased its share of the total energy consumption to about 42 percent by virtue of almost doubled production during the 20 years.

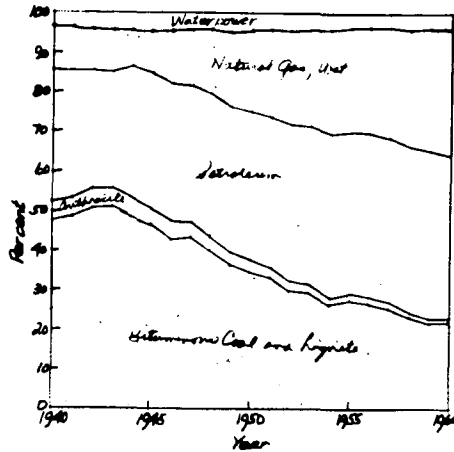


FIGURE 2. CONSUMPTION OF MINERAL FUELS AND WATER POWER IN U. S., 1940-1960

Natural gas, until the long gas pipelines were built, held quite steady at around 10 percent of the total. However, once there were means to distribute this gas, its convenience, cleanliness, and above all its low price led to remarkable gains. By 1960 gas was supplying almost one-third of our total energy consumption. Annual production rose from something under 4 trillion cubic feet in 1940 to 13 trillion cubic feet in 1960, a more than threefold increase. As we all know, this increase continued almost unabated for the next decade and led in large part to our present situation.

This then has been the pattern of the distribution of the energy load among our principal sources. It will perhaps be worthwhile to look at the situation for each one.

Figure 3 shows the story for coal production. No figure for reserves is shown because there are such wide variations depending on the basis for

the estimate. We have been assured by one of the power companies that we have more coal in the ground than the Arabs have oil. If this does not reassure us, then estimates ranging from 200 to 1000 years' supply should give some comfort.

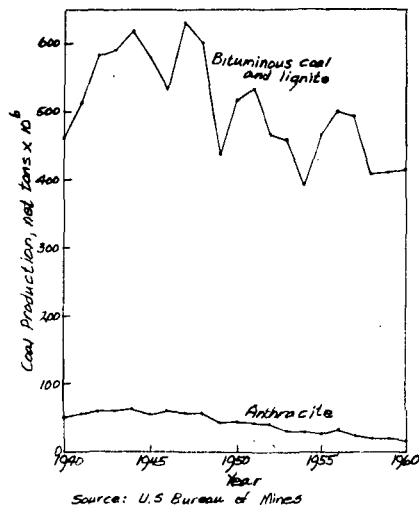


FIGURE 3. COAL PRODUCTION, 1940 TO 1960

The war and its aftermath gave some impetus to coal production, but the inroads of oil and gas began to show their effect and production of coal had decreased by almost one-third by 1960.

Figure 4 shows data on crude petroleum production. On this scale the sharp increase during the war is overshadowed by the continuing increase over the rest of the decade. World production, however, about 1950 began to show a tremendous rate of growth, doubling from 1950 to 1960. The U. S. share of world production dropped from over two-thirds to one-third.

Figure 5 shows the changes in world and U. S. reserves.

Known reserves in the U. S. showed a modest but steady growth throughout the period, but since production rose much more rapidly than new reserves, there was a significant decline in the reserves-to-production ratio.

The Middle East discoveries starting in 1950 began to grow at an almost unbelievable rate. From a little over 20 billion barrels in 1950, the estimated reserves rose to almost 200 billion barrels by 1960, a ten-fold increase in 10 years! After about 1957 reserves in other parts of the world began to increase also and the total world reserves rose to about 270 billion barrels.

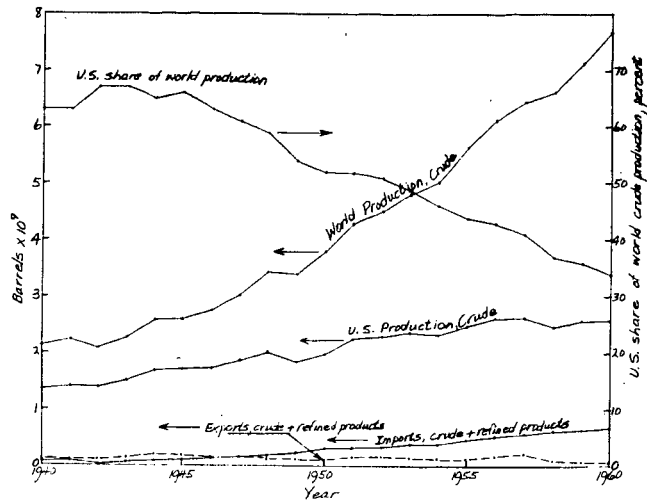


FIGURE 4. CRUDE PETROLEUM PRODUCTION

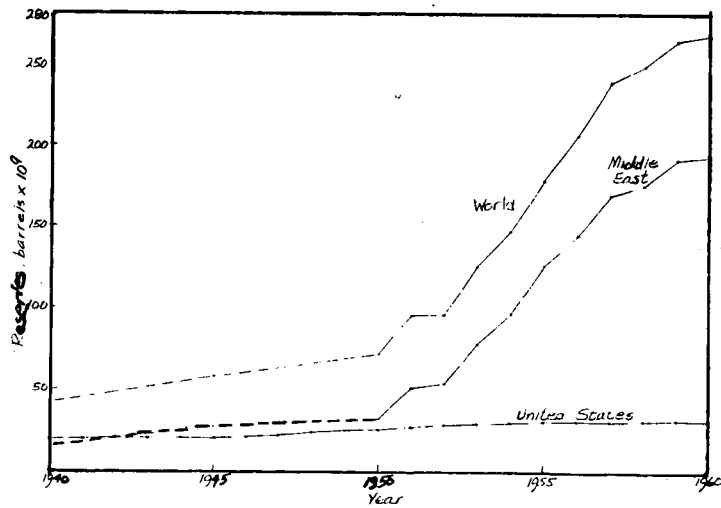


FIGURE 5. PETROLEUM RESERVES: FREE WORLD TOTAL, MIDDLE EAST, AND THE UNITED STATES, 1940 TO 1960

Figure 6 shows the history of gas during this period. In 1946 production was about 5 trillion cubic feet and by 1960 had risen to over 15 trillion cubic feet. However, for a number of reasons, the development of new reserves failed to keep pace with increases in production. In 1945 the ratio of reserves to annual production was over 30. By 1960 this had dropped to 20!

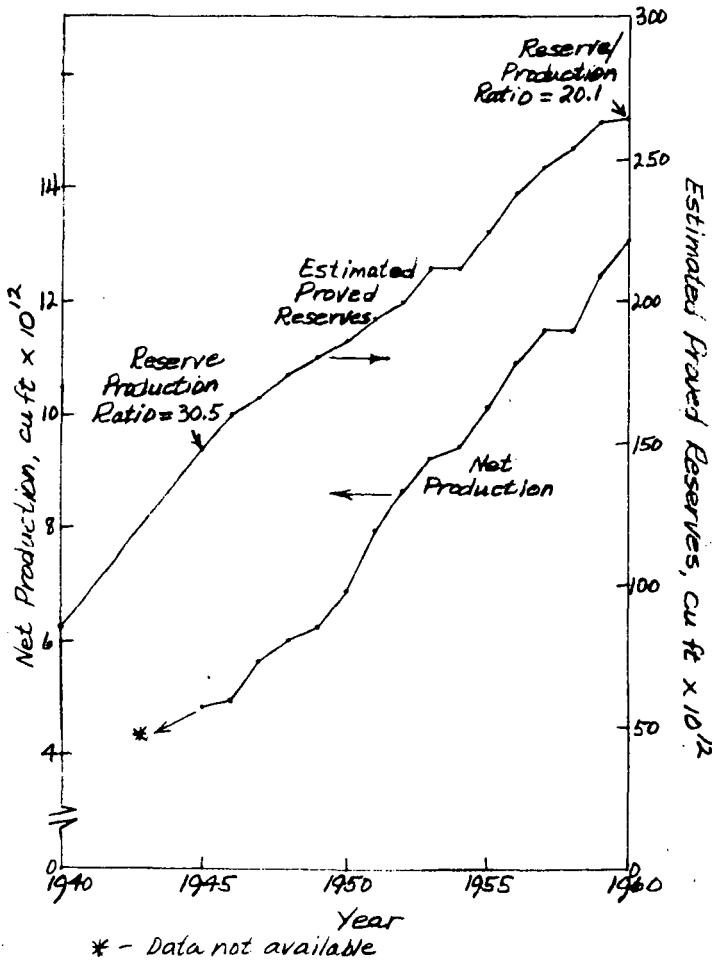


FIGURE 6. NATURAL GAS ESTIMATED PROVED RESERVES AND NET PRODUCTION, 1940 TO 1960

III. PRODUCTION OF LIQUID FUELS FROM COAL (1946-1953)

As noted above, the strong worry about postwar fuel supplies led to an almost complete dedication to solutions of the problems of producing synthetic fuel.

Not only was it necessary to develop coal hydrogenation processes, but also to develop the Fischer-Tropsch synthesis, the production of hydrogen and synthesis gas from coal, and finally the purification of those gases.

A. Coal Hydrogenation

In what seemed to be an emergency, the research and development work in the U. S. drew very heavily at the beginning on the information regarding German war-time activities. In the closing days of the war, British and U. S. Technical Oil Missions followed hard on the heels of the advancing armies, collecting documents, drawings, and intelligence concerning the top German men in the field who might be available for information and advice concerning the work in the U. S. and Great Britain. A considerable number of these men left Germany for England and the United States. Their contribution was significant.

German Practice. Germany used a variety of carbonaceous feedstocks in seven major plants. Detailed descriptions of these plants will not be attempted because of time limitations.

In general the coal was pulverized and made into a paste (50 percent coal) with a recycle heavy oil; catalyst was added and the paste preheated in the presence of some hydrogen as shown in Figure 7. The heated mixture passed through a series of three converters usually operating in the neighborhood of 900 F and 10,000 psi. By stepwise pressure letdown at the outlet, oil and gaseous product were separated and sent to the distillation system for recovery. The residue (ash, catalyst, unconverted coal, and the heaviest oil) was diluted with heavy oil, and centrifuged to recover as much oil as possible. The centrifuge residue was sent to coking kilns where additional oil was recovered and the solid residue was discarded.

The high-boiling portions of the product oil were vaporized and hydrogenated further over catalyst contained in a series of baskets in the vapor-phase converter as shown in Figure 8.* The character of the final products was determined by the amount of recycle and by the amount of hydrogen used. Any reasonable product mix was possible, but the lighter the product, the smaller the plant output and the greater the hydrogen consumption.

* At lower temperatures.

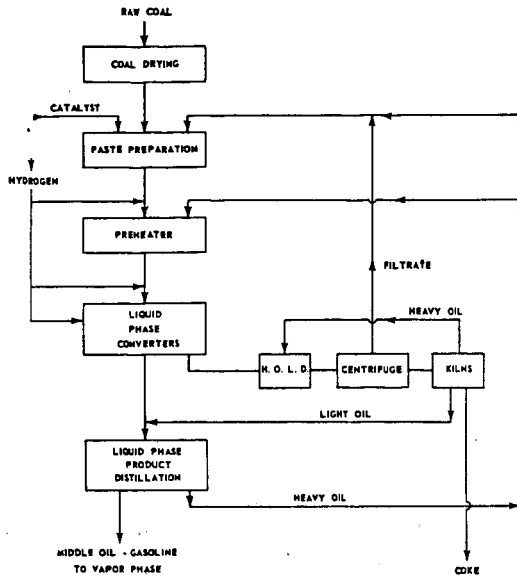


FIGURE 7. GENERAL SCHEME, LIQUID PHASE

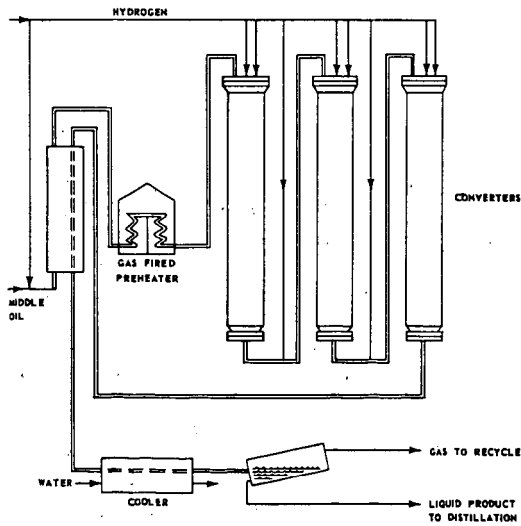


FIGURE 8. FLOW DIAGRAM, VAPOR PHASE

It should be borne in mind that although Germany produced over one-third of its total requirements by synthesis, this amounted to only 100,000 barrels per day. This may be compared with the 1973 consumption of 16-17 million barrels per day in the U. S.

U. S. Bureau of Mines Demonstration Plant. The construction of this plant was authorized by the Synthetic Liquid Fuels Act. The basis for the design was patterned after the German operations at Lutzkendorff and Welheim. The design was developed with the aim of applying modern U. S. engineering practices whenever such applications showed promise of increasing throughput or efficiency, promoting safety, or decreasing the cost of the gasoline product. The converters (2 liquid phase, one vapor phase) were 39 feet long and approximately 20 inches inside diameter. The plant was designed to charge just under 2 tons of coal per hour and to produce about 200 barrels per day. When the operations terminated in 1953, 2000 to 4000 tons each of four bituminous coals, one sub-bituminous coal, and one lignite had been processed.

The emphasis was on operability and, although, not all of the problems were successfully eliminated, a remarkable amount of progress had been made.

Bureau of Mines Pilot and Research Efforts. Research on coal hydrogenation started in the Bureau in 1936 and with the advent of the Synthetic Fuels Program a new laboratory was built at Bruceton, Pennsylvania. The bench-scale and pilot-plant research carried on here made a large contribution to the construction and operation of the demonstration plant. Studies were performed on new catalysts, catalyst preparation, effects of process variables, reaction mechanism, and other significant elements.

Activities in England. England had a commercial coal hydrogenation plant in operation in 1937. When war came, because of the bomb hazards, coal operations were terminated and the plant was used at lower pressures for the hydrogenation of creosote oils. Undoubtedly some research and development were carried on but references in the literature are scarce.

Union Carbide Company. The Union Carbide Company announced in 1952 the operation of its coal-hydrogenation plant at South Charleston, West Virginia. It was stated that the process would be aimed at the production of chemical raw materials and intermediates rather than liquid fuels from coal. Pressures were lower (6,000 psi maximum), temperatures lower, throughputs higher, and hydrogen consumption lower than in conventional liquid- and vapor-phase operations. A substantial part of the coal was liquefied to asphalt, and the announced intention was to feed this

to a unit for the production of metallurgical or specialty coke. The lighter products were to be processed to separate chemicals or classes of chemicals for sale or use as such. The unit was stated to have a design capacity of 300 tons of coal per day with the expectation that this could be increased as operating experience was gained.

Since operating conditions differed so widely from those actually required for gasoline production, this operation is not of direct interest in connection with synthetic fuels.

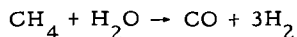
B. Fischer-Tropsch Synthesis

Work on the Fischer-Tropsch Synthesis had been carried out for many years in Germany and had been brought to commercial production, although on a limited scale.

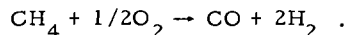
With the prospects of petroleum shortages in the U. S., interest in the process became widespread. In general, there were two basic approaches.

One was a high-temperature fluid bed synthesis aimed primarily at the production of gasoline. This was the path followed by the petroleum companies. Such a synthesis required a high ratio of hydrogen to carbon monoxide, to minimize deposition of carbon on the catalyst. In cases where cheap methane was available, the decomposition of methane with steam or oxygen was used as a source of synthesis gas.

The methane was reformed with steam:



or partial combustion with oxygen:



The hydrogen-to-carbon monoxide ratio was adjusted by water-gas shift if necessary to give the desired feed to the synthesis unit.

Construction of two commercial plants was started and one of these was put in operation. Little was published on the results except that the operation was not economically competitive at that time with gasoline from petroleum.

The second approach to liquid fuels from coal by the Fischer-Tropsch reaction was generally a compromise between the German operations and those contemplated by the oil companies. The coal was to be gasified as described below, the deleterious sulfur compounds removed, and the H_2 to CO ratio adjusted by the water-gas shift reaction, to produce the desired

feed to the synthesis unit. There were a goodly number of variations proposed each with its own advocates. Also, there was required a substantial study of the theoretical aspects of the process. The thermodynamics and kinetics of the various schemes were explored, and the work required was multiplied by the possibility of hot and cold gas recycle, additions of carbon dioxide or water to the feed, and a wide variety of means to remove the heat of reaction and to control temperatures. The search for new and improved catalysts also was pursued vigorously.

Undoubtedly much of the research and development related to the Fischer-Tropsch processes has never been reported, but the publications that did issue bear ample evidence of the large amounts of work that was done.

The Bureau of Mines Laboratories at Bruceton did much bench-scale and pilot-plant experimentation, and a demonstration plant was constructed and operated at Louisiana, Missouri. There still remained unsolved problems when the plant was shut down in 1953, but it is reasonable to believe that a reliable, sustained operation of this process could be achieved.

C. Coal Gasification

Whether coal hydrogenation or Fischer-Tropsch were used to make liquid fuels, hydrogen or synthesis gas would be needed in great quantities.

Petroleum consumption in the United States was in 1946 about 5 million barrels a day; if synthetic fuels were to make a significant contribution, outputs of 1/2 million barrels a day certainly could be visualized. Coal hydrogenation required about 8,000 cubic feet of hydrogen per barrel of liquid product, and the Fischer-Tropsch process required around 30,000 cubic feet of synthesis gas per barrel. Gas requirements then could range from 4 to 15 billion cubic feet per day, or 1.5 to 5 trillion cubic feet per year. On a volume basis, that is of the same order as the total natural gas production of the United States at that time.

Although it was proposed in some cases to make hydrogen or synthesis gas by reaction of methane with steam or oxygen, even in those days it was practical only if for some special reason methane was extremely low in price.

For most of the country, the source of synthesis gas or hydrogen must be coal, and the gasification of coal became the subject of very extensive investigation. If synthetic fuels were to be used widely, they must be produced in almost every part of the country and, if possible they must use coals locally available. This meant that the preferred gasification step should be one in which almost any coal was suitable. As is known today, this puts some very stringent restrictions on the gasification process.

Lignite seemed favorable because of its suspected higher reactivity, but the higher moisture and ash content, and the location of most of the lignite deposits did not make it attractive as the universal feed.

Much of the bituminous coal available in the heavily industrialized regions of the country was moderately or strongly caking, which difficulty would have to be overcome. In any case most of the coal-gasification process development work was aimed at a process that could use any coal as a feed.

Some processes operated at atmospheric pressure, but most were designed for operation at pressures that would permit gas purification and Fischer-Tropsch operations without further compression. For coal hydrogenation, compression costs would be substantially reduced with hydrogen at 300-400 psi instead of at atmospheric pressure.

Substantially all of the processes under investigation used oxygen and steam to gasify the coal. In the few attempts that were made to eliminate or minimize the use of oxygen, analyses showed that the economics were not favorable.

The surge of interest in this field can be illustrated by the United States patents granted on gasification processes. The following tabulation shows the number of patents granted whose application dates fall in the period indicated.

	<u>Number</u>
1930-1944 (avg/yr = 5.5)	77
1945	13
1946	25
1947	29
1948	28
1949	31

These figures apply only to United States patents.

It is not possible to discuss each of these many approaches. There are many literature references that describe them in detail and judging by the publications, many of the members of the Fuel Division at that time were heavily preoccupied with the problems of coal gasification. Except for the Bureau of Mines Synthetic Fuels Plant, and the Du Pont Company at Belle, West Virginia, most did not progress beyond a throughput of 100 to 500 pounds of coal per hour.

At Louisiana, Missouri, the Bureau was able to obtain a Linde-Franke oxygen plant with a production of 25 tons per day and the gasification section was designed on that basis. Coal was pulverized to about 80 percent through 200 mesh and transported by the oxygen to a Koppers-Totsek gasifier. Steam was preheated to about 2000 F in a pebble heater fired by natural gas.

The unit was a horizontal cylinder with steam, coal, and oxygen fed at each end and a gas offtake near the top center. After a waste heat boiler, the product was water scrubbed, passed through an electrostatic precipitator, and sent to the compressor or to atmospheric pressure storage.

The 2000 F steam superheat was to promote reaction and to reduce the oxygen demand. It was found that this was not economical and later operations in another unit used steam at 1000 F. The operation of these units was primarily experimental, and almost all of the gas supplied to the Fischer-Tropsch unit was made from coke in a Kerpely producer with steam-oxygen blast. (Operation of this process had been practiced for some years for the production of ammonia synthesis gas.)

The Du Pont Company installed a commercial-sized atmospheric coal-gasification unit in the plant at Belle, West Virginia, primarily for the production of hydrogen for ammonia synthesis. The design used was an outgrowth of their own development work, plus that of the Babcock and Wilcox Company in cooperation with the Bureau of Mines at Morgantown, West Virginia. The unit was designed for the production of 25 million cubic feet per day and is reported to have operated satisfactorily. No data have been published. After more than 2 years of use, operations were terminated in favor of the use of natural gas as a raw material.

Theoretical Studies. At the same time that the process development work was in progress, there was a large amount of research and development devoted to the thermodynamics and the kinetics of steam-coal-oxygen-synthesis gas systems. This work was essential to the design of the various gasifiers, it led to new gasifier concepts, and it led to means of increasing coal conversion and decreasing oxygen requirements.

D. Synthesis Gas Purification

The Fischer-Tropsch catalysts under investigation were in general very sensitive to sulfur poisoning, and much effort was devoted to purification of the synthesis gas from coal. Many commercial processes existed, but it was felt that further work would result in more efficient and economical processes. Except for that at Louisiana, Missouri, none of these newer approaches were placed in operation on a significant scale, but from the standpoint of fuel chemistry research and development, a considerable effort was expended.

IV. ADVENT OF INCREASED FOREIGN OIL SUPPLIES

Even as the United States was engaged in a major effort to develop oil supplies for our anticipated demand, the development began of new oil reserves in the Middle East and in Africa.

In 1951, the U. S. had a consumption of a little over 2 billion barrels per year and proven reserves of only 25 million barrels. Even at this low figure, only the Middle East showed more reserves, at about 50 billion barrels. World reserves were only 103 billion barrels.

By the end of 1961, proven U. S. reserves had increased to about 38 billion barrels and consumption had risen to over 3-1/2 billion barrels per year. Elsewhere, however, the situation was vastly different. The Middle East reserves had increased to almost 200 billion barrels, Russia's proven reserves were about equivalent to those of the U. S. Africa was beginning to be developed, as were other eastern hemisphere sources. New additions to reserves were being made in Canada, and in the Caribbean countries. World reserves had risen to 305 billion barrels in the face of rising consumption in the U. S. and in the rest of the world.

The increase in world reserves cast increasing doubt on the wisdom of continuing the urgent U. S. effort to develop synthetic liquid fuels. A change of administration in the U. S. added impetus to the movement to abandon this effort, and the Office of Synthetic Liquid Fuels was eliminated in 1953. The Demonstration Plants were shut down, laboratory staffs were reduced, and the research emphasis for those remaining was shifted to other lines of endeavor.

The programs of the Fuel Chemistry Division for the remainder of the decade reflected this change very quickly. Papers describing work on synthetic fuels almost disappeared, and other subjects began to replace them.

V. SITUATION IN 1960

At the end of 1960 then, we find the research in fuels chemistry focussed on much the same fields as in 1940. The upset occasioned by the effort on synthetic fuels had largely subsided and pressures associated with it had largely been relieved.

There were evidences of increasing concern regarding our diminishing domestic resources, especially with respect to natural gas. Some efforts

were being restarted on the gasification of coal and on the synthesis of pipeline-quality gas - but these were not extensive. Discussing this aspect further would probably carry this paper over into the realm of the following one.

Although the fields of fuels research generally were comparable to those in 1940, it does not mean that no progress was made during the 20 years. In spite of the war interruption, much fruitful work was done and our knowledge of the constitution, character, and utilization of fossil fuels had been advanced significantly.

ACKNOWLEDGEMENT

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ADVANCES IN FUEL CHEMISTRY 1961-74

G. Alex Mills

Assistant Director
Office of Coal Research
Washington, D.C.

I. OUR CHANGING FUEL SUPPLY/USE PATTERNS

The 1961-74 period has been characterized as one of greatly expanding energy use, an increase of over 65% occurring in the United States in this period. (Table 1 and Fig. 1) (1). However, more fundamentally, it has been a period of change, a reversal from abundant, cheap fuels to one of real and impending fuel shortage.

The character of the fuel use pattern has altered significantly, with growth greatest in use of fuels for transportation and for generation of electricity. A new factor of far reaching importance has been fuel use restrictions imposed for prevention of environmental degradation. These restraints have affected the fuel use pattern, for example, in switching from coal to oil for generation of electricity.

There has also been a change in the fossil fuel supply pattern. Gas now supplies 33%, petroleum 43% and coal 19% of our energy needs. A new national feature has been the recognition that coal and oil shale must become major suppliers of energy in the United States in the period 1985-2000 and beyond. A significant activity therefore has been the initiation of a greatly expanded effort in coal and oil shale research.

The 1961-74 period is also unusual in the initiation of tar sands exploitation and also of the use of nuclear energy for power use, the latter growing to about 2% of our energy spectrum.

The 1961-74 period has been characterized by the spectacular growth in petrochemicals, with many examples of innovative chemistry contributing to the success of new products and improved processes for chemicals, particularly in the plastics field.

The changing patterns of fuel use and fuel supply have interacted with fuel chemistry, in that new and improved chemical processes have satisfied a need or in other cases, provided a means or cause for changes. There have truly been a number of breakthroughs, mostly in petroleum chemistry, no doubt because of the much greater research effort in these areas. It can be confidently expected that synthetic fuels chemistry will provide breakthroughs in this area in the next few decades.

II. PETROLEUM CHEMISTRY

The greatly expanded use of petroleum has been reflected in an intensive search for new and improved refining process technology seeking to make better products and to provide higher efficiencies. Remarkable improvements have recently been achieved in several refining processes, despite their relative maturity (>25 years) and past research effort. Thus, means of obtaining greatly improved yields of desired products and suppression of unwanted products have been uncovered for catalytic cracking, reforming and hydrocracking. Improvements in hydrosulfurization, although perhaps not as spectacular, are important, especially in the ability to process heavy petroleum residua.

A. Hydrocarbon Chemistry. Advances in hydrocarbon chemistry were reviewed by Schmerling in 1972 as part of a comprehensive Petroleum Chemistry Symposium (2). He concluded that perhaps the most important advance in theoretical hydrocarbon chemistry during the past fifty years was the postulation that highly reactive intermediates were involved. Such intermediates can be free radicals, carbonium or carbanion ions or others such as carbenes. Catalytic surface complexes should also be included. Earlier work by Whitmore describing carbonium ions postulated an electron-deficient carbon atom, this deficiency inducing a migration giving rise to a rearranged product. More recently Olah (3) has suggested that two types of positive carbon ions exist: The classical trivalent ion and a pentacoordinated non-classical ion. The pentacoordinated ion is considered to consist of five atoms bound to a carbon atom by three single bonds and a two-electron three-center bond. Postulation of the pentacoordinated ion has many advantages in explanation of reaction mechanisms.

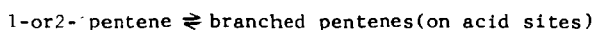
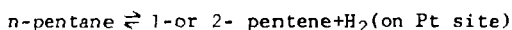
A very interesting catalytic reaction of olefins was described by Banks and Bailey in 1964 (4). They showed that alkenes undergo disproportionation to homologs of higher and lower molecular weight in the presence of alumina-supported molybdenum oxide, etc., at 100-200 degrees centigrade. Propylene, for example, was disproportionated to ethylene and n-butylenes at 94% efficiency at 43% conversion. The mechanism of the reaction may be considered to proceed by a four center ("quasicyclobutane") intermediate involving the four doubly-bonded carbon atoms of two molecules of olefin and catalyst.

Considerable progress has been made in alkali catalyst hydrocarbon reactions. The behavior of carban ions is remarkably different from that of carbonium ions. Alkyl groups in the former do not migrate. Primary carban ions are more stable than secondary ions which are more stable than tertiary. The reverse is true with carbonium ions. This leads to much different catalytic products.

B. Catalytic Reforming. Catalytic reforming of petroleum has taken great strides. The Free-World catalytic reforming capacity totals in excess of seven million barrels per day with about 50% of this capacity located within the United States and Canada. The bulk of the United States' capacity has been built during the last two decades in response to sharply increased demand, beginning about 1952, for high octane number gasolines needed to fuel high compression ratio, large-displacement engines.

Aromatics (benzene, toluene, and xylenes) are important components of the high octane reformate. The hydrogen produced as a "by-product" in reforming has become an increasingly valuable for use in associated hydrotreating and hydrocracking operations.

A significant advance was the recognition of the dual-function nature (isomerization and hydrogenation) of reforming catalysts (5). The mechanism of hydrocarbon reactions over such dual-function catalysts has been established and is illustrated for the isomerization of n-pentane (6).



Branched pentenes + $\text{H}_2 \rightleftharpoons$ isopentane (on Pt site). The amount of olefin present in the gas phase is extremely small because of the large excess of hydrogen used in the process and the moderate temperature and high pressure. It is important to recognize that dual-function catalysts can accomplish more than is achieved by passing reactants through two reactors in sequence, each filled with a different single-function catalyst (7).

As a result of mechanism studies and an understanding of the catalyst-hydrocarbon interaction, modifications of existing catalysts have been brought about. For example, improved selectivity has been achieved by changing the balance of functions.

Platinum-containing catalysts have dominated the field throughout the 1960's. Late in the 1960's several catalyst suppliers announced new catalysts which have come to be known as bimetallic. The early 1970's continued to show rapid development of additional bimetallic catalysts.

Bimetallic catalysts offer much higher activity and selectivity maintenance. The improved selectivity and activity permits operation at lower pressure and lower gas recycle ratios and/or higher severity.

The development of reforming catalysts capable of drastically improving performance represents potentially the most far-reaching improvement in catalytic reforming. These recent developments represent a "quantum jump" in catalyst performance (8).

The addition of rhenium to a platinum reforming catalyst results primarily in improving stability. Figure 2 shows data on Rheniforming a heavy naphtha at lower pressures (9). It has been suggested that some kind of platinum-rhenium couplet is involved, although it is now known

how this complex acts. Other metals and also sulfur are believed to have a beneficial effect. An important point is that platinum-rhenium do not per se lead to higher yields. However, higher yields can be achieved because such catalysts can operate at lower pressures where conventional reforming catalysts are not stable but at otherwise equivalent conditions, the initial yields are the same as those obtained with conventional catalysts.

C. Catalytic Cracking. A "quantum jump" improvement in catalytic cracking has also been achieved by the introduction of so-called crystalline aluminosilicate catalysts. The crystalline aluminosilicate, or zeolitic catalysts, are more active, more stable and produce considerably more of the desired products, gasoline and light fuel oil, compared to amorphous silica-alumina catalysts. They also produce considerably less undesirable products, coke and light gas.

The striking improvement in gasoline yield is evident from the following results (10).

Catalyst	Durabead(1) Amorphous	Durabead(5) Molecular Sieve
Yields Volume %, fresh feed		
Conversion	54.2	68.0
Heavy fuel	13.9	8.2
Light fuel	31.9	23.8
C ₅ +gasoline	39.9	53.1
Total C ₄ 's	13.3	14.7
Dry gas weight %	6.7	7.1
Coke weight %	3.5	4.8

Durabead 5, the first commercial zeolitic cracking catalyst was introduced in March 1962. Since that time a variety of other zeolitic catalysts have developed in both moving bed and fluid form. The zeolite catalysts now are used in over 90% of cracking units. The use of x and y zeolites with a pore size of about 10 Å has provided for even further improvements including very high activity. The ion exchanged faujasites can have cracking activities many orders of magnitude greater than silica-alumina (11). In turn, use of highly active catalysts have made possible process variations including riser cracking.

Crystalline zeolite are molecular sieves which have pores of uniform dimension of molecular size eg. 4 Å. Early concepts of molecular sieves as catalysts were to utilize them employing the concept of "shape selective" catalysts with pores which could accommodate molecules of certain molecular dimensions but exclude others, -eg. straight chain but not branched chain molecules. Actually, selective reactions were found possible (12), although later application for catalytic cracking using crystalline zeolites with pores in the 10 Å diameter have become the most significant application. While attention has been given to the unusual electronic charge fields in the pores of the zeolites to which reactant molecules are subject (13), much of the scientific basis of the catalytic action and selectivity of zeolites has not been resolved (14,15).

D. Hydrocracking. The decade of the 1960's witnessed the establishment of modern hydrocracking processes in petroleum refining. From a single demonstration unit of 1000 barrels per day capacity in 1960, commercial installations have grown to over 50 units with a capacity of about 800,000 barrels per day of total capacity. The demand for gasoline and middle distillates and the availability of low cost hydrogen have played major roles in their growth. The most significant factor has been the development of superior catalysts having excellent activity and activity maintenance at operating conditions far less severe than those used in the older hydrocracking processes.

Research is making available increasingly active and economical catalysts whose composition can be tailored to meet particular feed and product objectives.

The catalysts are dual-function catalysts having a critical balance. The chemistry of hydrocracking has been discussed and has been reviewed in terms of the balance of catalyst functions (16). (see also for references).

The "Paring" reaction is one of the most interesting new reactions discovered. As described (16), the products of hydrocracking hexamethylbenzene over a dual function catalyst are shown in Figure 3. The principle products are light isoparaffins and C_{10} and C_{11} methyl benzene. Essentially no ring cleavage occurs and hydrogenolysis to form methane is small. To account for the formation of isoparaffin products, a process of isomerization leading to side chain growth, followed by cracking of side chains of four or more hydrocarbons is proposed. The mechanism proposed is illustrated in Figure 4. Alkylcycloparaffins also exhibit the paring reaction.

E. Hydrodesulfurization. The desulfurization of petroleum is one of the most significant petroleum refining operations. With lighter petroleum fractions, desulfurization is important for subsequent catalytic refining steps eg. reforming. A new emphasis on the use of hydrodesulfurization particularly of heavy fuels has been imposed by the strict regulations for low sulfur content of boiler fuels, with an imposition of 0.8# SO_2 per million Btu (17) and even more strict regulations for some cities.

In 1960 there were about $2\frac{1}{2}$ million barrels per day of installed hydrotreating and hydrocracking capacity in the United States (about $\frac{1}{2}$ of oil processed). In 1971 this has grown to $5\frac{1}{2}$ million BPD or $\frac{1}{2}$ the 11 million BPD. Thus one of the remarkable features of hydrocracking is the rapid growth rate and high capacity reached. A second significant feature of commercial hydrotreating has been the application to heavier fractions including residua. The tag end of a heavy distillate with a 1050 degree F end-point may have a molecular weight of 800-900. Much of the sulfur in these cuts is present as substituted benzo and dibenzo thiophenes (18). Residua fractions contain asphaltenes present as highly dispersed colloidal material with an average molecular weight of roughly 5,000 to 10,000. To remove sulfur from such materials - more difficult because of molecular

structure - requires higher severity of hydrodesulfurization. This means raising the temperature, where other bonds will begin to break.

It is of interest to study the asphaltene molecule, where a structure shown in figure 5 has been postulated (19). The aromatic sheets are about 14 Å across and there are 4 or 5 sheets per stack. It is structures of this type which must be desulfurized.

The chemistry of hydrodesulfurization is only partially understood. Several excellent reviews have appeared (20, 21, 22, 23). Most researchers believe that for thiophene the reaction proceeds in two steps, the first producing butylene and hydrogen sulfide, and the second in which butylene is hydrogenated to butane. However, it is pointed out that the first step must be complex and proceeds through a butadiene intermediate. Much of the mechanism studies have been published by Beuther and co-workers.

Cobalt molybdate and nickel molybdate catalysts are used extensively. Relatively little is known how they act. In operation the active components exist as lower valence sulfides. Nickel-tungsten sulfides were used by the Germans. Diffusional effects are important.

The tolerance of catalysts to metals (N_1 and V from porphyrins) is important in maintaining catalyst life.

F. Other Petroleum Processes. Other developments have occurred in hydrocarbon alkylation, polymerization, isomerization and dehydrogenation. There have been many innovations in the chemistry of petrochemical manufacture. These are outside the scope of this review.

III. TAR SANDS

An historic event during the 1961-74 period was the initiation of commercial production of oil from the Canadian tar sands. This began in 1967 in a plant designed to produce 45,000 barrels per day. The Athabasca sands cover 12,000 square miles and contain 600 billion barrels of oil in place. The plant built by the Great Canadian Oil Sands Company is based on a four-stage sequence of mining, materials handling, extraction and heavy oil upgrading (24). Extraction is by a hot water system. The heavy oil is processed in delayed coke drums. The overhead is separated into three streams: naphtha, kerosene and heavy gas oil. These streams are hydrogenated individually and then blended to form a product called synthetic crude. While many unusual mining situations are encountered, the processing of the tar is by previously known petroleum refining techniques, although now applied to an unusual material. The separation of the tar from the sand by hot water processing has presented an important surface chemical field. A second 80,000 barrels per day plant has been proposed with several different process steps, many of them in the mining and conveying (25).

In clearing the primary oil, a thermal dehydration-cyclone arrangement will take the place of a dilution-centrifuge system.

In primary conversion, hydrovisbreaking will replace delayed coking. Again, the innovation is in the application of refining to the tar sands.

The chemical constitution of tar sands has been characterized further using modern analytical tools, including the nature of the sulfur compounds (26, 27).

IV. OIL SHALE

Oil Shale is an important potential source of fossil fuel in the United States in amount being second only to coal as a resource. The potential estimated from the Green River formation is between 600 (high grade over 25 gallons per ton of rock) and 1,800 (total) billion barrels of oil. Most of the oil shale is on federal lands. An unsuccessful attempt was made in 1968 to lease a few selected tracts. However, events so changed that a second program of leasing in 1973 of four tracts of about 5,000 acres each, has met with highly competitive bidding, the winning bids on the four tracts amounting to nearly \$500,000,000.

Over the years, most technical effort has concerned mining of the oil shale and various mechanical means of retorting it. Retorting of the oil shale has been carried on a fairly large experimental scale of about 1,000 tons per day, employing several different types of retorts (28). A demonstration plant began operation in Brazil using direct fired shale calcination. Burning of oil shale for power generation continued in Europe.

The chemical nature of shale oil has been further defined, as shown in the following table (29).

INSPECTION DATA ON TYPICAL SHALE OIL CRUDE

Gravity API	19.8
Pourpoint °F	83.5
N wt.%	2.1
S wt.%	0.7
O wt.%	1.7
C wt.%	83.9
H wt.%	11.4
Conradson Carbon	4.7
Bromine No.	33.2
Sediment wt.%	0.04
Ni ppm	6.4
V ppm	6.0
Flash °F	108.
Molecular wt.	328.

Investigations of the structure of kerogen are difficult because kerogen is a large complex molecule belonging to the multipolymer class, its insoluble nature and its inhomogeneity. Colorado oil shale of the Green River formation contains about 16% insoluble organic matter called "Kerogen." This represents about 4/5 of the organic matter present. The other 1/5 soluble organic matter represents "soluble bitumen." Using a combination of micro-pyrochromatography, separation and mass spectrometry, provided a structure for kerogen shown in figure 6 (30). X-ray diffraction has also been used for determination of the structure of kerogen (31).

In situ production of oil shale has shown promise. There are potential advantages both from avoidance of mining costs and a lessening of possible environmental damage. In situ tests at Rock Springs provided a crude shale oil which has been characterized and its conversion into an oil suitable for refining in a petroleum refinery demonstrated (32, 33). Recently, the press has reported tests for in situ shale oil production in which a cavern corresponding to a fraction eg. 25% of oil shale is removed, the oil shale above it fractured to form a permeable rubble, and the whole shaft then calcined to drive off the shale oil with improved economics.

The fracturing of the oil shale with chemical explosives has been described (34). It was shown that the explosion will propagate in water-filled natural fractures and sand propped, hydraulically induced fractures in oil shale. The shale was fragmented by this method and a successful underground retorting experiment to recover shale oil was performed.

The use of nuclear detonation has also been proposed. An interesting proposal is the bioleaching of oil shale and experiments have shown promise (35).

The hydrogasification of oil shale has been described. It was shown that the presence of hydrogen, even low pressure, significantly increases the organic carbon deposit compared with hydrogen-free retorting (36).

Studies on the chemical nature of kerogen showed the feasibility of using kerogen as a natural raw material for the synthesis of monomers, not by traditional pyrolytic methods, but by direct chemical processing resulting in the scission of native polymethylene chains, structural elements of the natural polymer, in the form of mono-acid and preferably dicarboxylic acids (37). Conventional industrial oxidants have been found to be suitable for direct oxidative destruction of the kerogen to saturated dicarboxylic acids. Kerogen treated with nitric acid and molecular oxygen yields 55% of $C_4 - C_{10}$ dicarboxylic acids.

In certain oil shale zones, the rock contains appreciable percentages of potentially valuable saline minerals. Trona ($Na_2CO_3 \cdot NaHCO_3$), associated with oil shale, occurs in vast quantities in Wyoming's Green River basin. In Colorado nahcolite ($NaHCO_3$) and dawsonite ($NaAlCO_3(OH)_2$) have been discovered in a zone 700 feet thick, also associated with oil shale.

Environmental protection and water usage continue to be of great concern in oil shale processing. Spent shale has been found to have properties similar to low quality cement, enhancing its disposal in compact fills. It can also be made to support vegetation. Disposal areas must be designed to prevent leaching of soluble minerals.

V. COAL

During the period 1961-74 scientific progress was made in further elucidating the structure of coal, using modern instrumentation, and in establishing the factors involved in chemical reactivity of coal. On the applied side, major efforts were made in developing chemical processes to remove sulfur dioxide from products of coal combustion (stack gas scrubbing). Over \$200 million has been spent in such installations in power plants in what must still be regarded as an experimental program.

A. Coal Gasification (38-42). For the most part, the gasification processes under development are closely related to the technology developed in the 1930's. In general the chemistry of high temperature gasification reactions remains the same for all processes. It is the mechanical and engineering variations which characterize the processes, particularly those features for supplying heat for the endothermic $C+H_2O$ reaction.

The required heat can be furnished by any of several methods: partial combustion of coal with oxygen, by electrical energy, by inert heat carrier, heat released by reacting CO_2 with metal oxide, or use of nuclear heat. Four large coal gasification pilot plants are in operation or are being constructed in the United States. Each involves fluid bed operation in contrast to the so-called fixed bed design of the Lurgi process which is in use in Europe. These four processes do involve certain novel chemical features. In the IGT Hygas process (hydrogasification), char formed in the process is reacted with steam using electrical energy as the heat source. The gas so formed, rich in H_2 and low in CO_2 is reacted with pretreated coal to produce a gas with high methane content. Since the hydrogen content of coal (averaging about 5 wt. %) is very low compared to that of methane (25%) coal gasification consists chemically of adding hydrogen to coal. In addition S, N and O constituents are converted to H_2S , NH_3 and H_2O respectively. The Hydrane process also converts coal to methane by hydrogasification.

Perhaps the most novel process in pilot plant stage is the CO_2 acceptor process. This process utilizes the reaction between hot lime (CaO) and CO_2 to furnish the required gasification heat. By use of a separate regeneration vessel, air is used instead of oxygen as in the Synthane or Bigas process.

One unique feature of the Synthane process is the use of a "tube-wall" reactor for methanation. The catalyst is a Raney nickel applied to heat exchange tubes by a flame spraying technique. This provides for highly effective heat transfer system. Another unusual methanation technique is provided by a liquid phase catalysis system.

The ideal gasification reaction for gasification of carbon is $C + 2H_2O \rightleftharpoons CH_4 + CO_2$, which is balanced chemically and nearly so calorimetrically. However, because the steam-carbon reaction does not proceed fast enough at lower temperatures, the reaction is carried out at 900 degrees C or above. Attempts have been made to operate at lower temperatures by catalysing the carbon-steam reaction, with partial success. One intriguing fact is the known capability of micro-organisms to convert cellulose to $CO_2 + CH_4$ at ambient temperature. While cellulose is somewhat different from coal, lignite can have an oxygen content of more than 20%.

The use of nuclear heat for coal gasification has been of considerable interest and is being actively investigated in Germany.

The in-situ gasification of coal is once again being tested experimentally in the United States since it offers many potential advantages.

There are other novel coal gasification processes in the research stage. The molten salt process and self-agglomerating process are further examples.

Interest has increased tremendously in coal gasification in recent years. The symposia reference (42), provide detailed information. Also, research needs have been critically analysed (43).

B. Coal Liquefaction. The conversion of coal to liquids can be carried out by four generic procedures.

1. pyrolysis to produce a gas, liquid and char
2. "solvent refining"--actually involving the transfer of hydrogen from a hydrogen "donor" organic molecule with some additional hydrogenation catalyzed by coal ash constituents
3. Fischer - Tropsch synthesis in which coal is converted to $CO + H_2$ which are then reacted to form hydrocarbon and alcohols
4. Direct catalytic hydrogenation

Several large pilot plants have been constructed recently in the United States to test new technology and several more are planned.

At the present time, the FMC Corp., under sponsorship of the Office of Coal Research, is operating a large COED (Coal Oil Energy Development) pilot plant with fluid bed pyrolysis (44). Powdered coal is subjected to increased temperatures in four successive fluid beds. Volatile liquid products are withdrawn at each stage and hence not subjected to the highest temperature where further cracking would occur. In this way maximum liquid yields are obtained.

Another type of process begins by treating coal with a hydrogen-donor solvent. There are several promising processes of this type under development in the United States (45). Broadly speaking, two categories are possible, those in which liquid extraction is carried out in a separate first step, and those in which extraction is carried out in the presence of a catalyst and under hydrogen pressure. The operation at Cresap by Consolidation Coal Company (44), and sponsored by OCR is of the first category; the hydrogen-donor solvent is hydrogenated in a separate step so as to regenerate its solvent capabilities.

Solvent refined coal. The dissolution of coal by organic agents under elevated pressure and temperature has long been known. German chemists Pott and Broche found a mixture of tetralin, phenol, and naphthalene to be the most satisfactory for bituminous coal. A key feature is that tetralin is a hydroaromatic "donor" able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism that is not accelerated by the pressure or hydrofining or cracking catalysts.

A pilot plant processing 6 tons of coal per day built by industry began operating in 1974 using a solvent refining process. The PAMCO solvent-refined coal process developed by Pittsburgh and Midway Coal Mining Company consists of mixing pulverized coal with a coal-derived solvent having a 500 degrees to 800 degrees F boiling range, passing the mixture with hydrogen through a preheater and reactor at about 1000 psi, separating the hydrogen plus hydrogen sulfide and light hydrocarbons formed, filtering the solution, flash evaporating the solvent and recovering the solidified coal product. The chemical analysis of charge and product is shown below. During the reaction phase, hydrogen reacts with part of the organic sulfur compounds forming the hydrogen sulfide. The hydrogen also stabilizes the solubilized coal products. The pyritic sulfur leaves the process in the filtration step, as does the other ash components.

	Kentucky No. 11 coal	Refined coal
Ash	6.9	0.1
C	71.3	89.2
H	5.3	5.0
N	0.9	1.3
S	3.3	1.0
O	12.3	4.4
Btu/lb	13,978	15,956
Melting point degrees C	----	128

Under the sponsorship of OCR a large pilot plant has been authorized for construction and operation in the State of Washington. This plant to start in 1974 will not only test scale-up factors, but will also produce sufficient product for larger scale testing of its combustion characteristics.

Scientists at the Bureau of Mines discovered that using a mixture of $(\text{CO}+\text{H}_2\text{O})$, or $(\text{CO}+\text{H}_2\text{O}+\text{H}_2)$ is even more effective than using H_2 alone for hydrogenation. The mechanism is related to the shift reaction $(\text{CO}+\text{H}_2\text{O} \rightleftharpoons \text{H}_2+\text{CO}_2)$ during which the hydrogen at an intermediate stage, possibly as the formate ion, is in a particularly reactive state. It should be possible to test the use of synthesis gas plus steam as an improvement in the solvent refined coal process.

H-coal process. The H-Coal process utilizes an ebullated bed reactor system developed by Hydrocarbon Research Inc. A unique feature of this reactor system is the ability to operate a catalyst system continuously with a feed consisting of solids, liquids, and gases. The upward flow of the feed maintains the catalysts in a state of rapid motion and permits the continuous passage of unconverted coal and ash from the reactor. Catalyst can be added and removed from the reactor during operation.

The production of low-sulfur fuel oil from coal by the H-Coal process has been discussed (47). It is stated that processing conditions can be varied to attain 1.5 to 1.0% S without ash removal, 0.5% S with ash removal and increased conversion severity, and 0.25% S with secondary treatment of part of the product.

For example, processing an Illinois No. 6 bituminous coal 3.6 bbls of C_4 + liquids were made/ton dry coal at 93% coal conversion. The sulfur content of the coal was 3.4% and of the liquids was 0.5%.

Turbulent catalytic reaction. In experiments conducted at the Bureau of Mines (48), a high-sulfur bituminous coal suspended in oil derived from coal was converted to a low-sulfur fuel oil by continuous processing through a fixed bed of pelletized cobalt molybdate alumina catalyst, under conditions of highly turbulent flow or hydrogen to prevent obstruction of the flow and to promote catalytic contact. From coal having 3.0% sulfur and 9.4% ash, the totally coal-derived centrifuged synthetic fuel oil, produced at 2000 psi and 850 degrees F had 0.31% sulfur and 1.3% ash. The data indicated that more selective separation of unconverted residual coal would provide fuel oils with sulfur content as low as 0.1% sulfur because the bulk of the sulfur is in the benaene-insoluble fraction of the product oil.

The new catalytic concepts for direct hydrogenation was previously reviewed (45, 49), references are detailed. A list of the systems is given below.

NEW HYDROGENATION CATALYTIC SYSTEMS

"Nascent"-active hydrogen generated in situ

Complexes of transition metals

Massive amounts of halide catalysts

Organic hydrogen donor solvents

Alkali metals

- (a) With H_2
- (b) With amines
- (c) Electrocatalytic

Reductive alkylation

Miscellaneous

Active hydrogen generated in situ. A combination of carbon monoxide and steam can hydrogenate coal more rapidly and to a greater degree than does hydrogen itself under the same conditions of temperature and pressure. The suggestion has been made that hydrogen, generated in situ by the water gas shift reaction between CO and H_2O , is in an activated form. It has also been suggested that the mechanism is via a formate ion.

Complexes of transition metals. Certainly one of the most, if not the most, significant development in the field of catalysis in recent years has been the discovery of a variety of new, and often unusual, catalytic reactions of transition metals and coordination complexes. The catalytic properties depend upon the central ion and the number and character of ligands. Some of these catalysts are soluble and have therefore been called homogeneous catalysts. Knowledge of their electronic structure has enabled the establishing of catalytic mechanisms on a molecular basis.

The capability of such metal-ligands complexes to react with hydrogen to form active species and the existence of coordinatively unsaturated metal complexes are fundamental to the mechanism of their reactivity.

One of the earliest and most important examples of their type of catalysts is cobalt carbonyl which, in the presence of $CO+H_2$, is capable of hydroformylating olefins. Cobalt carbonyl is also active in hydrogenating certain aromatic compounds and coal. Dicobalt octacarbonyl, in the presence of carbon monoxide and hydrogen, functions as a selective homogeneous hydrogenation catalyst for polynuclear aromatic hydrocarbons.

Coal was also treated with $CO+H_2$ in the presence of dicobalt octacarbonyl at the same temperature, 200 degrees C. Both H_2 and CO were added to coal under these conditions. Thus, this is one of the most active catalytic systems ever observed for coal hydrogenation.

Massive amounts of halide catalysts. The use of halide catalysts in amounts comparable to the coal or polynuclear hydrocarbons used has given some unusual hydrocracking results. Comparison of a $SnCl_2$ /coal ratio of 0.01 and 1.0 illustrates that while about 85% of the coal was converted to benzene solubles in each instance, the asphaltene conversion--the difficult step--was nearly completed with the larger amount of catalyst. Similarly, large amounts of zinc chloride were effective, and this compound was superior to conventional hydrocracking catalysts for coal or coal extract. Zinc chloride gave more rapid reaction, more complete conversion than conventional catalysts, and a very high octane without reforming.

Compared with conventional catalysts, molten zinc chloride more than doubled the conversion and hydrogen consumption when using a hydrocracking residue as feed stock, even though a lower temperature was used. Note-worthy also, is the high selectivity of the process for production of gaso-line and the high ration of isoparaffins to normal paraffins.

Hydrogen donor. The solution of coal by extraction using organic agents under pressure has long been known, and a vast literature exists. The German chemists, Pott and Brosche, found that a mixture of tetralin, phenol, and naphthalene was the most satisfactory solvent for bituminous coal. A key feature is the presence of tetralin which is a hydroaromatic "donor," able to transfer hydrogen to coal. This transfer is by a thermal, free-radical mechanism. The structure of the donor is important. The function of the phenol is apparently to assist in pulling the hydrogenated coal into solution. This combination effect is demonstrated in the table below where, it is seen, the synergistic effect can be built into a single molecule, o-cyclohexylphenol. The process mechanism is complicated. For example, much of the oxygen is eliminated in making the coal soluble.

LIQUEFACTION OF BITUMINOUS COAL BY HYDROGEN DONOR SOLVENT*

<u>Vehicle</u>	<u>% Liquefaction</u>
Naphthalene	25
Cresol	32
Tetralin	50
o-Cyclohexylphenol	82

* 0.5 Hr. at 400 degrees C.

Alkali metals. The alkali metals can act in hydrogenation of coal in several related ways: (a) as a direct hydrogenation catalyst (with molecular H_2), (b) with amines, and (c) in a catalytic electrochemical reduction.

Reductive alkylation. The formation of aromatic hydrocarbon anions is made possible by reaction with alkali metals. For example, naphthalene, dissolved in hexamethylphosphoramide, reacts with one or two moles of lithium to form the mono- or dianion. In turn, the dianion can react with CH_3I to give 9,10-dimethyl 9,10-dihydroanthracene. This is called reductive alkylation, since one of the aromatic nuclei is converted to an alkylated dihydrobenzene.

Reductive alkylation can also be carried out with coal substance. Although only 3% soluble in HMPA, coal became 90% soluble on addition of lithium to a suspension of coal in HMPA. Alkylation of coal with ethyl iodide-yielded an ethylated coal which was 35% soluble in benzene at room temperature. It was estimated that the alkylation corresponds to 1 alkyl to 5 carbon atoms. Reductive alkylation is also a means of adding hydrogen,

in that H/C of coal is increased. This alkylation method is much more effective in causing solubility of coal than addition of an equal number of hydrogen atoms. Moreover, a degree of benzene solubility is achieved which is not possible by hydrogenation.

The alkylation of coal was not restricted to use of HMPA. Coal can be readily alkylated in tetrahydrofuran, provided a small amount of naphthalene is added which acts as an electron-transfer agent.

Other novel hydrogenation systems. There are a number of other novel hydrogenation systems. These include volatile catalysts such as iodine, dehydrogenation of coal to form hydrogen (9000 ft³/ton) which possibly could be combined in a dehydrogenation-hydrogenation disproportionation process, use of molecular sieves containing metals to bring about hydrogenation of selected molecules, high-energy modification of coal or catalysts, use of ultrasonics to increase coal solubilization.

C. Combustion. Space does not permit the review of advances in the chemistry of combustion. Important new knowledge has been obtained which relates to combustion control for prevention of pollution. Thus it is possible to control combustion in a manner which minimizes NO_x formation, of particular importance in coal combustion. Likewise, the use of limestone addition in combustion for removal of SO₂ may become of major practical importance in developing fluid bed combustion. The chemical removal of SO₂ from stack gases is an alternative to synthetic fuels from coal in many large installations (50). The competition between synthetic fuels and stack gas scrubbing promises to become even more important and both processes are economically dependent on future advances in their respective technology (51).

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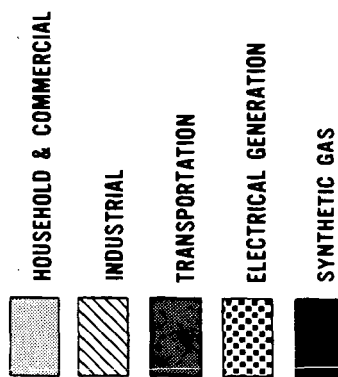
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UNITED STATES ENERGY CONSUMPTION BY SECTOR 1971 - 2000

(QUADRILLION BTU's)



USE SECTORS	1961	1971
Household & Commercial	10.4	14.3
Industrial	14.6	20.3
Transportation	11.0	17.0
Electrical Generation	8.5	17.4
Total	44.5	69.0

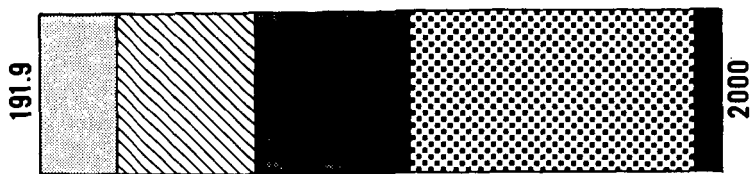
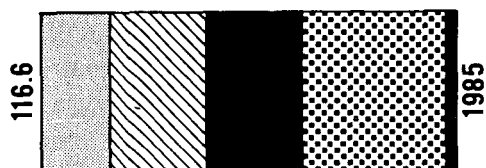
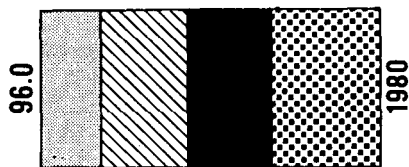
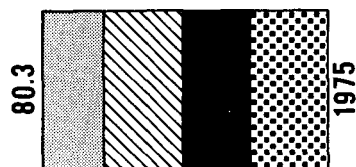
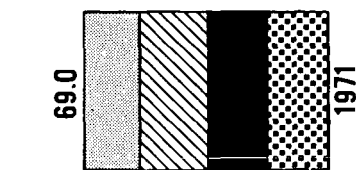
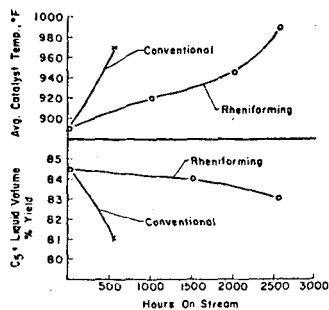


Fig. 1

Fig. 2



Rheniforming of 420°F Isomax naphtha.

Fig. 3

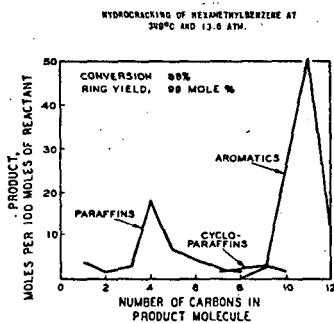
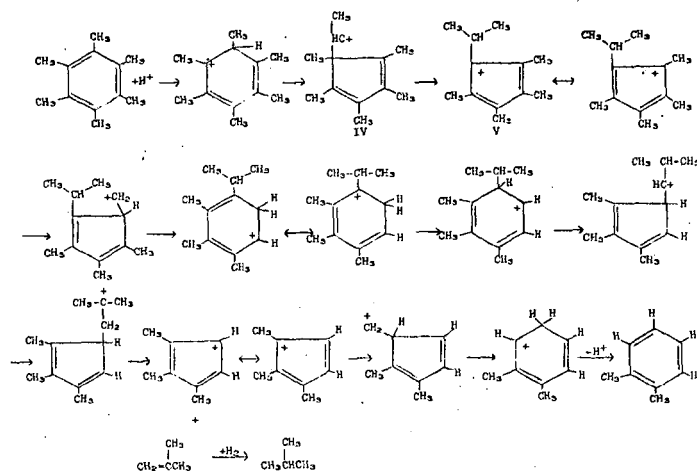


Fig. 4



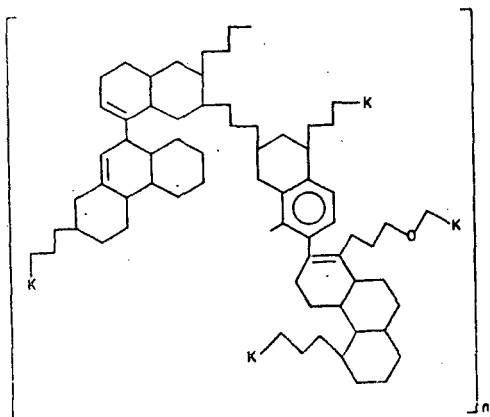
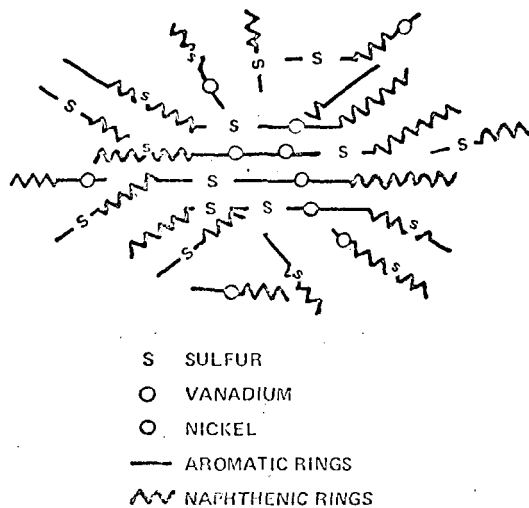


Fig. 6

Generalized Structure of Kerogen of the Green River Formation

Table 1.—United States total gross consumption of energy resources by major sources,¹ 1947-70 revised, and 1971 preliminary

Year	(Trillion Btu)							Percentage change from prior year
	Anthracite	Bituminous coal and lignite	Natural gas dry ²	Petroleum ³	Total fossil fuels	Hydropower ⁴	Nuclear power ⁴	Total gross energy inputs
1947	1,224	14,600	4,518	11,367	31,709	1,326	--	33,035
1948	1,275	13,622	5,033	12,557	32,487	1,393	--	33,880
1949	968	11,673	5,289	12,119	30,039	1,449	--	31,488
1950	1,013	11,900	6,150	13,489	32,552	1,440	--	33,992
1951	940	12,285	7,248	14,848	35,321	1,454	--	36,775
1952	897	10,971	7,760	15,334	34,962	1,496	--	36,458
1953	711	11,182	8,156	16,098	36,147	1,439	--	37,586
1954	683	9,512	8,548	16,132	34,875	1,388	--	36,263
1955	599	10,941	9,232	17,524	38,296	1,407	--	39,703
1956	610	11,142	9,834	18,627	40,213	1,487	--	41,700
1957	528	10,640	10,418	18,570	40,154	1,551	1	41,706
1958	483	9,366	10,995	19,214	40,068	1,636	2	41,696
1959	478	9,332	11,990	19,747	41,547	1,591	2	43,140
1960	447	9,693	12,699	20,067	42,906	1,657	6	44,569
1961	404	9,502	13,228	20,487	43,621	1,680	18	45,319
1962	363	9,826	14,121	21,267	45,577	1,821	24	47,422
1963	361	10,353	14,843	21,950	47,507	1,767	34	49,308
1964	365	10,899	15,648	22,386	49,298	1,907	35	51,240
1965	328	11,580	16,098	23,241	51,247	2,058	38	53,343
1966	290	12,206	17,393	24,394	54,282	2,073	57	56,412
1967	274	11,982	18,250	25,335	55,841	2,344	80	58,265
1968	268	12,401	19,580	27,062	59,291	2,342	130	61,763
1969	224	12,509	21,020	28,421	62,174	2,659	146	64,979
1970	210	12,712	22,029	29,614	64,565	2,650	229	67,444
1971	186	11,857	22,819	30,570	68,698	2,862	404	68,698
1972	150	12,345	23,125	32,966	68,586	2,946	576	72,108
1973	140	13,380	23,558	34,689	71,767	2,941	853	75,561

¹ Gross energy is that contained in all types of commercial energy at the time it is incorporated in the economy, whether the energy is produced domestically or imported. Gross energy comprises inputs of primary fuels (or their derivatives), and outputs of hydropower and nuclear power converted to theoretical energy inputs. Gross energy includes the energy used for the production, processing, and transportation of energy proper.

² Excludes natural gas liquids.

³ Petroleum products including still gas, liquefied refinery gas, and natural gas liquids.

⁴ Outputs of hydropower (adjusted for net imports or net exports) and nuclear power converted to theoretical energy inputs calculated from national average heat rates for fossil-fueled steam-electric plants provided by the Federal Power Commission. Energy input for nuclear power in 1971 is converted at an average heat rate of 10,660 Btu per net kilowatt-hour based on information from the Atomic Energy Commission. Excludes inputs for power generated by nonutility fuel-burning plants, which are included within the other consuming sectors.